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# Chemistry and Chemiluminescence of Certain 1,1'-Biisoquinolinium Salts

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## ABSTRACT

The syntheses of various 1,1'-biisoquinoline derivatives and salts are described; some of the unusual chemistry encountered in the preparative effort is discussed.

When aqueous or alcoholic solutions of these 1,1'-biisoquinolinium salts are made basic while exposed to air, bright chemiluminescence occurs. The intensity and duration of the light depends on the particular salt. Oxidation products have been isolated, their structures determined, and their fluorescence correlated with the light emitted during chemiluminescence. A mechanism has been proposed for the oxyluminescence reaction which involves reduction of the biisoquinolinium dication by hydroxide or alkoxide ion to an air-reactive, electron-rich olefin. Oxidation-reduction potentials for the dication--ion radical--olefin system have been determined.

Chemiluminescence quantum yields have been measured, and factored into fluorescence efficiencies and chemical efficiencies.

# Naval Weapons Center
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## FOREWORD

The use of various chemiluminescent materials to provide relatively low-level illumination has made a significant contribution to nighttime military combat and rescue operations. These materials may be used for target marking, for identification of landing zones, for marking supply containers to be air-dropped at night, for providing emergency illumination in aircraft cockpits in case of power failure, and for a wide variety of other applications where a short-term light source is required.

Research programs have been conducted at the Naval Weapons Center in support of the Navy's interest in these materials and their applications to provide and improve formulations of chemiluminescent materials for test purposes. The properties of available formulations are studied and recommendations for their use are made. While emphasis is directed toward getting brighter compositions, appropriate consideration is also given to chemical stability, physical properties, and other characteristics necessary for field applications.

Chemiluminescent systems based on two different principles have been investigated and developed: (1) binary, an example of which is the oxalate ester-hydrogen peroxide-fluorescer system ("Chemlite", "Oxalume"); and (2) air-reactive, as typified by the earlier formulations utilizing tetrakisdimethylaminoethylene (TMAE).

The desirability for an improved air-reactive chemiluminescent system comparable in light output to the best binary one, has led to the investigation of other air-oxidizable materials. Certain biisoquinolinium salts constitute one of the more promising classes of such compounds, and investigations on their preparation and properties are continuing. Several aspects of these research efforts are described in the following open-literature publications, reprints or copies of which are included here:

1. "Chemiluminescence of 3,3',4,4'-Tetrahydro-1,1'-Biisoquinolinium Salts," by Ronald A. Henry and Carl A. Heller (*Journal of Luminescence*).

2. "Chemiluminescence: Quantum Yields for Luminol and a Biiso-quinolinium Salt," by Carl A. Heller, Donald T. Carlisle and Ronald A. Henry (*Journal of Luminescence*).

3. "Reactions of Epimeric 2,2'-Diacetyl-1,1',2,2'-tetrahydro-1,1'-biisoquinolines," by Ronald A. Henry, Arnold T. Nielsen and Donald W. Moore (*Journal of Organic Chemistry*).

4. "Intramolecular Cyclization of N-Alkyl-3,3',4,4'-tetrahydro-1,1'-biisoquinolinium Salts," by Ronald A. Henry and Donald W. Moore (*Journal of Organic Chemistry*).

5. "The Chemiluminescent Autoxidation of Reduced Biisoquinolinium Dications," by Carl A. Heller, Ronald A. Henry and John M. Fritsch (*As presented at 1972 International Conference on Chemiluminescence and to be published in "Chemiluminescence and Bioluminescence," Plenum Press, New York (1973).*

Some related work can be found in NWC TP-5163, May 1971.

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*Chemistry Division*
6 February 1973

Under authority of
HUGH W. HUNTER, *Head*
*Research Department*

# CHEMILUMINESCENCE OF 3,3',4,4'-TETRAHYDRO-1,1'-BIISOQUINOLINIUM SALTS

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Basic methanolic solutions of 2,2'-dimethyl–3,3',4,4'-tetrahydro-1,1'-biisoquinolinium iodide (1) chemiluminesce brightly when exposed to oxygen. The first reaction is between base and dication to form a mixture of olefins. These electron-rich olefins are formed by proton removal from, or RO⁻ addition to, the dication and subsequent redox equilibria. The olefins react with ground state $O_2$ by another redox reaction involving ROH as catalyst. Several oxygenated products are formed and several emission peaks appear. One correlation between a product and an emission peak is possible.

The synthesis and some properties of several new salts are described. The oxyluminescence of 1 is compared briefly with that of previously reported compounds.

## 1. Introduction

Recently Mason and Roberts[1] described the chemiluminescence of diquaternary salts derived from 1,1'-biisoquinoline (BIQ). These BIQ salts, when made basic in alcohol or water solutions, react with oxygen. The chemistry appeared to be simple and the system a reasonable one to study mechanistically.

During synthesis of Mason and Roberts' compounds in this laboratory, another closely related chemiluminescer with a much slower oxidation rate was discovered. The chemistry of this new compound, 2,2'-dimethyl–3,3',4,4'-tetrahydro-1,1'-biisoquinolinium diiodide (1), will be discussed in this paper and will be compared briefly with that for compounds 2 and 3[1].
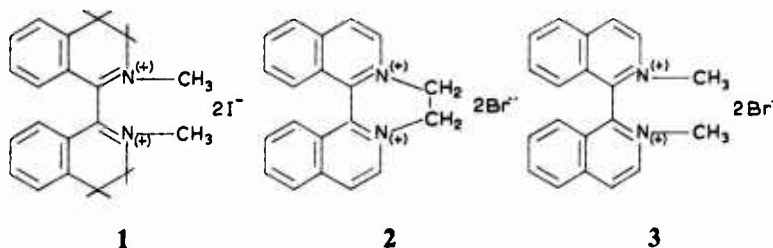
Mason and Roberts reported that a red color appeared when a solution of 2 was made basic *in vacuo*. This color disappeared with chemiluminescence when $O_2$ diffused into the solution. They proposed a bis anhydro base for this colored intermediate although the structure of the oxidation product did not support this proposal. Finally, the chemiluminescence spectrum was reported to match the fluorescence spectrum of the oxidation product 4.



**4**
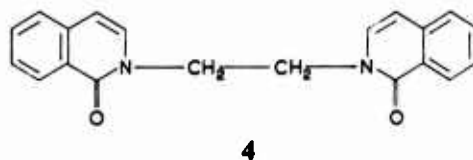
This study will be seen to support many of the findings and suggestions of Mason and Roberts. However, the oxidation and chemiluminescence of 1 appear to be more complex than that of 2[1, 2]). Some of the results, though, help explain the oxyluminescence of the BIQ salts and show parallels to N,N'-dimethyl–9,9'-biacridinium dinitrate (lucigenin)[3, 4]) and tetrakis-dimethylaminoethylene (TMAE)[5]).

## 2. Results and discussion

### 2.1. SYNTHESIS

3,3',4,4'-Tetrahydro–1,1'-biisoquinoline, 5, which is an intermediate in the most satisfactory route to 1,1'-biisoquinoline*, can be prepared from N,N'-bis (β-phenylethyl) oxamide in 70% yield (crude product) by a modified Bischler-Napieralski synthesis. Methyl iodide and 5 react rapidly in aceto-



**5**
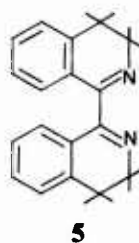
nitrile at room temperature to give the monomethiodide**, even when the former is present in excess. Prolonged refluxing in either absolute ethanol or acetonitrile is required to effect conversion to the dimethiodide, 1.

Other alkylating agents have been examined. Both the mono- and di-

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* We are indebted to Dr. S. F. Mason for details about the synthesis of this compound.
** This compound in methanol shows a very faint purple chemiluminescence of short duration when made basic in air.

ethiodides have been prepared; their behavior is similar to that of the methiodides. With either benzyl or phenacyl bromide in acetonitrile the mono quaternary salt was formed readily at room temperature; both salts gave a faint purple chemiluminescence in methanol when made basic. In contrast to the reaction of 1,1-biisoquinoline with ethylene dibromide to give 2, 5 and ethylene dibromide at 130–135°C reacted to furnish a dark, resinous product which was difficult to purify. Some 1,2-bis(3,3',4,4'-tetrahydro–1,1'-biisoquinolyl-2)–ethane dihydrobromide was present; 2 was also formed, possibly as a result of air oxidation of the tetrahydro–biisoquinoline since the alkylation was not performed in an inert atmosphere. Similar products were also formed when equal molar quantities of 5 and ethylene dibromide were reacted in acetonitrile at room temperature.

## 2.2. OXIDATION PRODUCTS

When methanol solutions of 1 exposed to air are made basic, there is an immediate, intense burst of purple light, followed by a less intense output of several minutes duration. In an attempt to define the oxyluminescing species, some of the oxidation products from this reaction were isolated and identified, and, for those which were fluorescent, their spectra compared with the chemiluminescence emission (spectral results are discussed below). The principal, ether–soluble product (50%) is 2-methyl–3,4-dihydroisoquinolone-1 (6) analogous to 4 recovered by Mason and Roberts from 2. However, a substantial quantity (38%) of a substitution product, 2-methoxy-methylene–3,4-dihydroisoquinolone-1 (7) is formed. Neither is fluorescent.



6         7
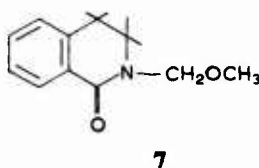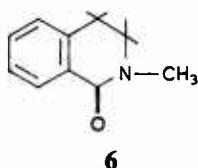
Small amounts of 2-methylisoquinolone-1 (8) and 3,4-dihydroisoquinoline (9) are also present. A mixture of oxidation products, poorly soluble in



8         9
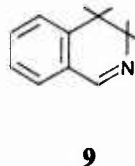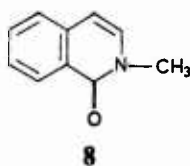
ether, was recovered and partially separated for mass spectrometric analysis. The mass spectra suggest the interesting point that the 1,1'-bond of the

biisoquinoline derivative was not cleaved in at least one product ($m/e$ = 362 parent).

The same oxidation products arise when the reaction is performed in 50% aqueous methanol; however, the amount of **7** present is substantially reduced.

## 2.3. NATURE OF OXIDIZABLE SPECIES IN SOLUTION

When an aqueous solution of **1** is made basic under air, there is little or no chemiluminescence probably because a red, oxidizable intermediate precipitates from solution. A mass spectrum on material freshly prepared under nitrogen is consistent with **10** ($m/e$ = 290, parent; the next peak at $m/e$ = 275 corresponds to M–CH$_3$), which represents a two electron reduction of the cation of **1**. This red precipitate, dissolved in methanol under nitrogen, has absorption peaks near 462 and 340 nm and when excited at 460 nm, a broad emission with a peak at 527 nm is observed. Upon exposure to air the absorptions disappear and a low intensity chemiluminescence results. Simultaneously a new fluorescence emission at 459 nm with an excitation peak at 333 nm (similar to that observed with **1** in methanol) appears.



**10**                    **11**                    **12**
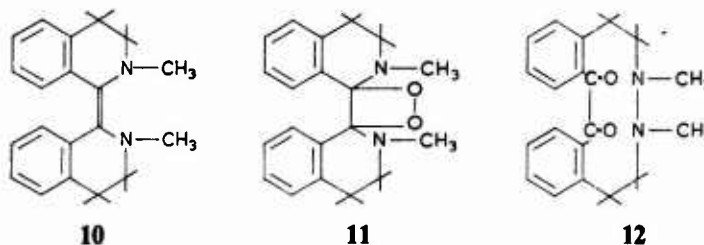
Oxidation of **10**, via several steps (see mechanism section below), would furnish the dioxetane **11**. Cleavage of **11** in a manner analogous to that reported for the formation of tetramethylurea in the oxidation of tetrakis(dimethylamino)ethylene (TMAE)[6, 7] would lead to **6**. Similar reactions are the formation of 1,3-diphenylimidazolidone-2 from bis-[1,3-diphenylimidazolidinylidene-(2)][8] and of N-methylacridone from 10,10′-dimethyl–9,9′-biacridinium nitrate[9]. If (**11**) were to cleave homolytically along a path analogous to the one offered by Urry and Sh⌐ ⁚o[7ᵃ] to explain the formation of tetramethyloxamide and tetramethylhydrazine in the oxidation of TMAE, then a product like **12** might result.

The reduction of **1** to **10** in basic medium demands that some component be oxidized. This can be accomplished at the expense of protons on either the methyl group or the methylene groups in the ring, and would account for the appearance of **8** and **9** in the products. Related examples of reduction by RO⁻ have been reported for an octamethyloxamidinium salt[7ᵃ] and for

1,1'-dimethyl–4,4'-bipyridylium dichloride[7b, c]); various mechanisms have been suggested.

The formation of the methoxy-substituted product, **7**, in methanolic solutions can be explained as follows



**13a**        **13b**        **14**
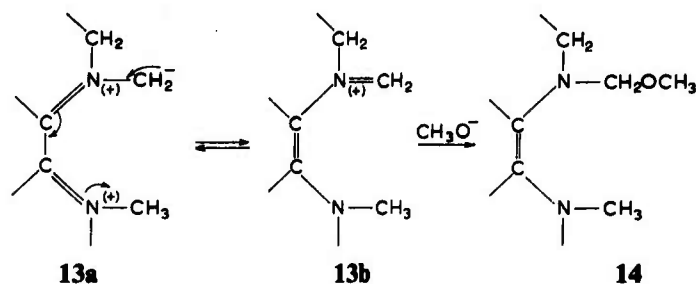
Oxidation of **14** in a fashion similar to **10** would furnish one molecule of **6** and one of **7**. The pseudo-base **14** could come from **13b** in a reaction analogous to the known conversion of 3,4-dihydro–2-alkyl-isoquinolinium salts to pseudobases by nucleophiles.

Product **8** could arise either through oxidation of **6**, or through the oxidation of some intermediate like **15**, which could be formed from a species similar to **13** where the proton has been removed from a ring methylene adjacent to nitrogen.



**15**
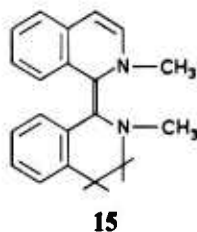
In solution all of the reduced forms can be in equilibria, via ion-radical intermediates, with the oxidized forms, the position of equilibrium depending on the respective oxidation reduction potentials; for example,



**16**        **17**
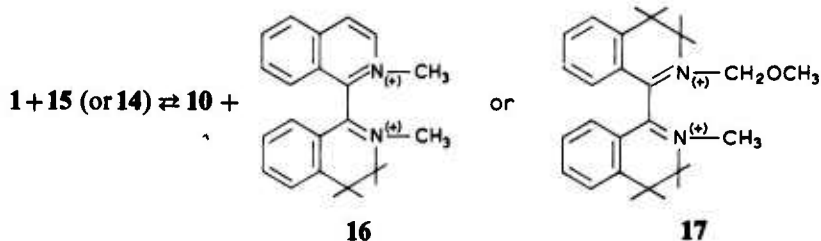
The oxidation–reduction processes proposed above gain additional support from the following experiment: When **1** in methanol under nitrogen is made basic with sodium methoxide (absorption peaks develop near 462 and 340 mm) and the solution allowed to stand for several hours, a mass spectrum on the recovered mixture of intermediates not only shows a peak at $m/e = 290$, again corresponding to **10**, but new peaks at $m/e = 288, 320$ and 350. The former corresponds to **15**, the latter two to mono-methoxy (**14**) and di-methoxy substitution products of **10**, respectively. The color of the solution of **1** is probably due in part to radical-ions which are involved in the equilibria since EPR studies show a radical present in red colored solutions of **2** under $N_2$.

The ease of oxidation of the reduction products should be given by the reduction potentials of the corresponding ions. A single sweep polarographic technique using methanol or aqueous solutions gave a complex series of reduction potentials. However, cyclic voltammetry in acetonitrile using about 0.2 millimolar solutions of BIQ salt and 0.2 M tetraethylammonium

TABLE 1

Reduction voltages

|   | First | Second |
|---|-------|--------|
| **1** | − 0.20 | − 0.40 |
| **2** | − 0.156 | − 0.52 |
| **3** | − 0.56 | − 0.66 |

perchlorate as supporting electrolyte gave the results in table 1. All the dications undergo "two resolved textbook type, one electron reductions"[10]). The first step produces a stable, red colored, radical-cation.

## 2.4. RATE AND EFFICIENCY OF LIGHT OUTPUT

Fig. 1 shows a typical run obtained when $O_2$ is added to basic solutions of the BIQ salts **1, 2,** or **3**. The ratio of the two peaks varies with oxygen pressure, with storage time of the solutions, and with the compound. With **2** the reaction time is limited to several minutes and the light disappears completely. With **1** a very low light level continues for hours.

This behavior is consistent with the equilibrium mixture of species which was found in the basic solutions. Each species can oxidize at its own rate since the interspecies equilibria is slow relative to the oxidation rate. At least two species must oxidize with luminescence. One explanation for the slow oxyluminescence of **1** is that the equilibrium between olefins and cations
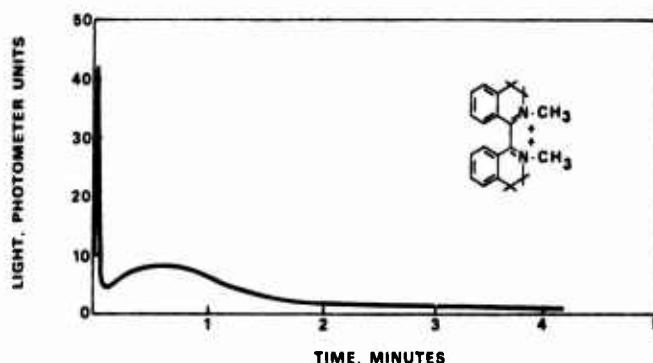
Fig. 1. Chemiluminescence of a premixed solution of BIQ salt **1** ($10^{-4}$ M) and sodium methoxide ($10^{-2}$ M) in methanol. $O_2$ added at time zero; $P_{O_2} \simeq 150$ torr. Two ml sample in 25 mm diameter vessel and well stirred during reaction.

must, with this compound, lie to the side of the cations. As the oxygen reactive species are removed by autoxidation more are produced slowly from the remaining **1** dication.

The relative quantum efficiency of **1, 2,** and **3** can be obtained by measuring the area under the curves. Table 2 gives a comparison of the three compounds at two concentrations. The areas were only measured for limited times so the long, low tail for **1** is missed. The initial chemiluminescence

TABLE 2

Relative light output from three BIQ salts

| Salt | [Salt] | [NaOMe] | Light |
|------|--------|---------|-------|
| 1 | $10^{-3}$ | $10^{-1}$ | 1.1 |
| 2 | $10^{-3}$ | $10^{-1}$ | 100 |
| 3 | $10^{-3}$ | $10^{-1}$ | 0.85 |
| 1 | $10^{-4}$ | $10^{-2}$ | 0.03 |
| 3 | $10^{-4}$ | $10^{-2}$ | 0.002 |

All runs at 0°C, 150 torr of $O_2$ and in methanol.

spectrum of all salts peak near 385 nm, where the detector's spectral sensitivity is quite flat, so that the uncorrected detector response is a valid comparison. The values in table 2 are for basic solutions which have stood several days under nitrogen. This is important since the amount of light which is produced when the solutions are ultimately exposed to air increases during storage as the BIQ salt plus methoxide solution approaches equilibrium. For salt **2** in particular, color changes are also noted during this period of equilibration.

The values of table 2 are not accurate since only a few runs were made and air leaks were possible. However, the relative efficiencies undoubtedly decrease in order **2**, **1**, and **3**. It appears to us that **2** with an absolute quantum efficiency[2]) close to 0.5 % will be the best compound for further mechanistic studies.

### 2.5. CHEMILUMINESCENCE SPECTRA

Flow runs permitted measurements of the spectrum within 10 sec of mixing aerated methanol solutions of base and BIQ salt **1**. There was thus little time for the complex equilibria to be established. Fig. 2 shows two spectra taken from identical solutions. The emission peak is at $385 \pm 3$ nm ($26\,000$ cm$^{-1}$ or 74 kcal einstein$^{-1}$).
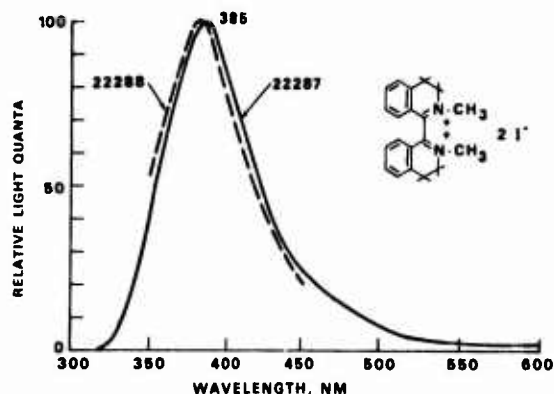


Fig. 2. Chemiluminescent emission spectrum in flow system about 9 sec after mixing. Solvent, anhydrous methanol saturated with dry air. Solution #1: (1), $1.05 \times 10^{-4}$ M. Solution #2: Sodium methoxide, 0.0109 M. Mixture ratio of #1/#2 about 0.5. Mixture flow rate 0.59 ml sec$^{-1}$. Slit 25 nm. Luminescence mode with $\times$ 10 amplification. Two different experiments.

Static runs were made with the same solutions used for the time runs of fig. 1. The initial flash seems to peak below 385 nm but is too rapid to give a good spectrum. Later spectra are shown in fig. 3. With time several new peaks appear near 415, 480, and 575 nm shifting the emissions to longer wavelengths. The longer wavelength peaks are stronger for higher initial concentrations of **1**.

It seems clear that the initial flash of fig. 1 is due to the excited species emitting at 385 nm although even this need not be a primary excited species[11]). The second broad peak must begin to show the spectral shift either because a new primary excited species is produced, or because of energy transfer or
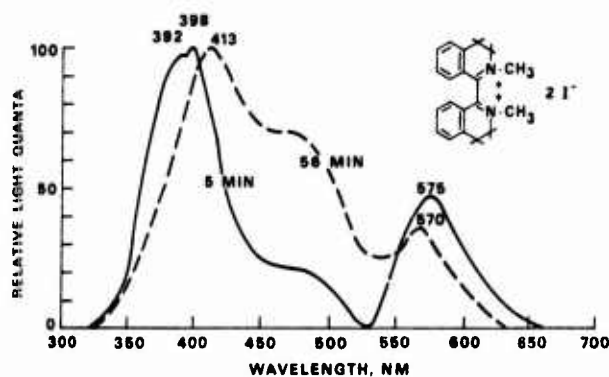
Fig. 3. Shift of chemiluminescence spectrum with reaction time. Anhydrous methanol; 1, 5 × 10⁻³ M; sodium methoxide, $5 \pm 1 \times 10^{-2}$ M. Saturated with moist air (25 % RH) at time zero and during run by shaking cell. 25 nm slit. Scan time about 2 min. Spectra normalized. The real peak height, at equal settings, decreased from 1.0 to 0.52 during the interval 5 to 56 min.

excimer formation reactions. These solutions are colored a faint pink (see below), but the spectral shifts in fig. 3 are not due to the fading of this weak color.

## 2.6. FLUORESCENCE SPECTRA

Fluorescence spectra were obtained from reaction mixtures and from isolated products in an attempt to unravel the complicated spectral shifts of the chemiluminescence.

The initial chemiluminescence emission peak of fig. 1 is probably due to 8 although we could never obtain a chemiluminescence spectrum showing the identical features of the fluorescence spectrum shown in fig. 4. This inability was undoubtedly due to experimental difficulties. At the dwell times for our flow cell the initial emission is already shifted by later peaks as seen in fig. 3. Smaller flow cells and shorter dwell times gave too little light. Thus, the spectra in fig. 2 with a peak at 385 nm is the closest we could come to a wide slit fluorescence peak of 378 nm for 8. With compound 2 there is more light and we can easily obtain chemiluminescence spectra with a 2.5 nm slit showing the same shape as fluorescence spectra despite a simile shift of emission peaks with time. We think a faster spectrometer will show the same thing for 1.

We took fluorescence spectra of reacting samples of 1. During the run we could identify 1 itself (fig. 5) until it slowly disappeared. Excitation at 325 nm then showed 8. Excitation at 245 or 375 nm gave a broad photoluminescence around 475 nm which looked like a mixture of simple spectra.
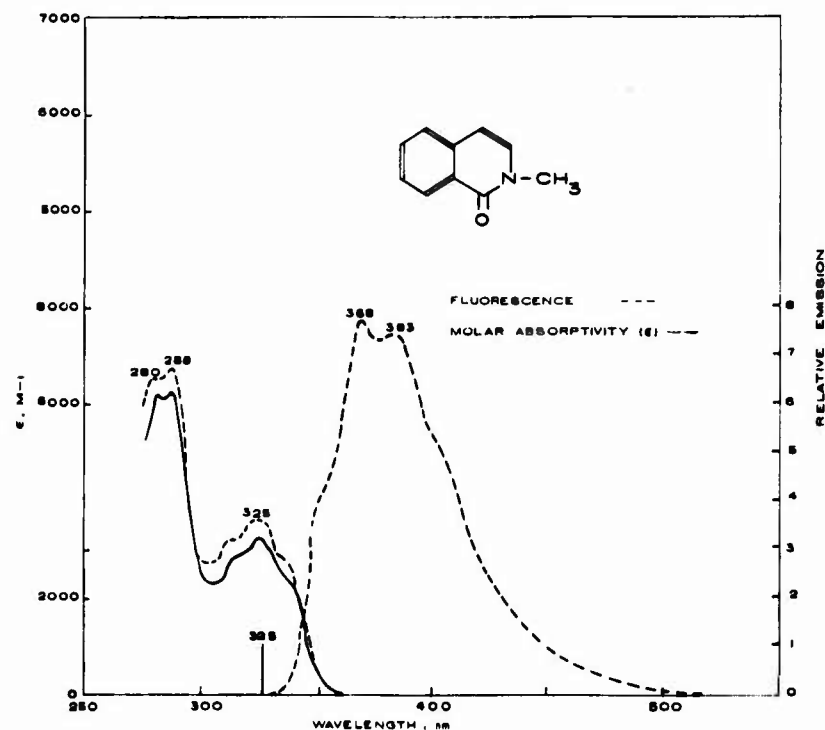
Fig. 4. Fluorescence emission and excitation spectra and absorption spectrum of **8**. Absorbance and emission (excited at 325 nm) measured at $8.00 \times 10^{-5}$ M using 2.5 nm slit. Excitation (monitored at 375 nm emission) measured at $6.02 \times 10^{-6}$ M using 2.5 nm excitation slit. Emission spectra at $4.3 \times 10^{-4}$ M showed no excimer bands. Solvent: methanol at 25 °C. Most concentrated solution made using 1.7 mg from glc separation, dissolved in 25 ml.

As stated above, the major products, **6** and **7**, were isolated and are not fluorescent. Two minor products other than **8** were isolated in quantities large enough for fluorescence measurements, but too small to weight or identify. These had fluorescence peaks at 385 nm and 498 nm (fig. 6) and could account for part of the observed chemiluminescence emission. However, it seems likely that some of the emission is from chemically produced "excimers" which do not exist as stable products nor form during photo-excitation at our concentrations.

Product **8**, the most likely candidate for the initial emission, was examined in some detail. It was a strong enough emitter so that traces in **6** and **7** made them appear fluorescent*. Its quantum yield was measured versus quinine

* We wish to thank a reviewer who convinced us that **6** and **7** could not fluoresce. When traces of **8** were removed this proved indeed true.
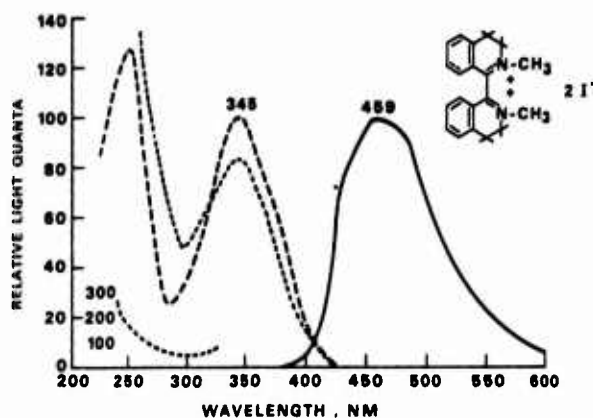
Fig. 5. Absorption (dotted curve), excitation (dashed curve) and fluorescence (solid curve) emission spectra for 1. All in air saturated methanol at 25°C. Concentrations: absorption $2.13 \times 10^{-5}$ M; excitation $2.8 \times 10^{-6}$ M; emission $2.13 \times 10^{-5}$ M. Slit 2.5 nm for all spectra.
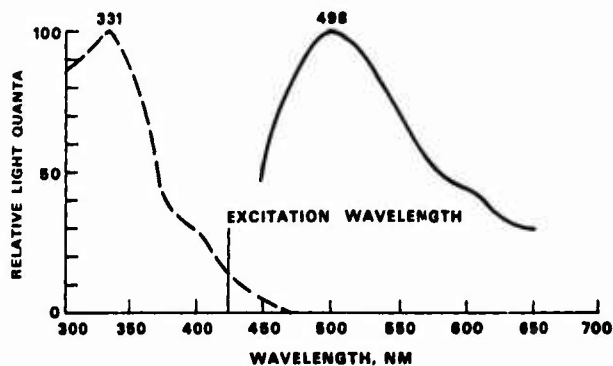


Fig. 6. Fluorescence emission and excitation spectra of oxidation product. Concentration in methanol unknown.

bisulfate on the Turner Spectro Fluorometer[12]). Under air the yield was 0.054. Quenching by air of other 1-isoquinolones is about 20%[2]), so the unquenched yield is estimated to be 0.07. Fig. 4 summarizes the absorbance and excitation data on 8. We also looked at the emission of 8 in the presence of $10^{-3}$ M 6 and 7. There were no new bands nor band shift attributable to mixed excimers.

Summarizing we think the initial fast reaction forms 8. Slower reactions of different intermediates form more than one minor product. These products are possibly formed as mixed excimers, emit and then decompose to the stable, final products. Possibly 6 and 7 are involved in the mixed excimers.

It seemed undesirable to try to further unravel the complications of this compound.

## 2.7. MECHANISM

The present observations permit a partial mechanism to be written for the initial fast reaction forming **8**. It seems possible the slow reactions may follow a similar path. The rates of each reaction may depend upon the equilibrium of the following reaction (where I is an olefin such as **10** and $I^{++}$ is the corresponding dication)

$$I + O_2 + ROH \rightleftharpoons I^{++} + HO_2^- + RO^-$$
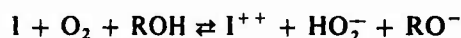
One evidence for such an equilibrium is the appearance of the fluorescence spectrum of the dication of **1** when $O_2$ is added to a soluti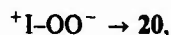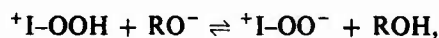on of **10**. Another is the thermodynamics[5]) of the reaction based upon the electrochemical studies. Unlike the case with TMAE[5]) these BIQ equilibria should lie to the left. Therefore, alcohols are required in higher concentrations to drive the reaction at reasonable rates. The equilibrium constants would be different for each species of olefin produced by the reaction of **1** with methoxide anion. This in part would account for the two reaction curves of fig. 1.

The peroxy anion produced in the above reaction could then react with dications as shown below. The series of reactions leading to excited isoquinolones probably follows the path postulated for many chemiluminescent reactions[14]):

$$I^{++} + HO_2^- \rightleftharpoons {}^+I\text{-OOH},$$

$${}^+I\text{-OOH} + RO^- \rightleftharpoons {}^+I\text{-OO}^- + ROH,$$

$${}^+I\text{-OO}^- \rightarrow 20,$$

$$20 \rightarrow \text{Isoquinolone-1}^*.$$
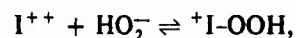
The species, $^+I\text{-OOH}(18)$, $^+I\text{-OO}^-(19)$, **20**, can be drawn with the reasonable central structures



| 18 | 19 | 20 |
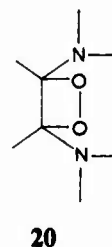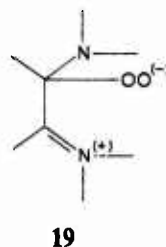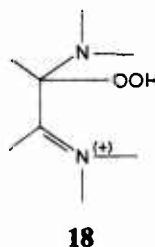
There will be a mixture of reactions since OOH⁻ when formed can react with any dication present. Certainly, $Na_2O_2$ added to BIQ salts gives a very rapid reaction although neutral $H_2O_2$ gives no luminescence.

With TMAE[5, 11, 13]) the dioxetane corresponding to **20** was very unstable, but the ionic intermediates could be frozen out at $-78\,^\circ$C or observed while decaying if $O_2$ was removed at $25\,^\circ$C. With other chemiluminescent molecules bridged peroxides and dioxetanes have proven to be relatively stable[14-17]).

With BIQ's **1** or **2** we have been unable to freeze out any intermediates. When $O_2$ is removed the reaction mixture immediately goes dark. Thus, the intermediates must all be relatively unstable and short-lived.

### 3. Experimental

#### 3.1. 3,3′4,4′-TETRAHYDRO–1,1′-BIISOQUINOLINE-5

Recrystallized N,N′-bis(β-phenethyl)oxamide (75.5 g), 75 ml of 1,1,2,2-tetrachloroethane, 150 g of phosphorous pentoxide, and 230 ml of phosphorous oxychloride were refluxed with very vigorous stirring for 1.5 hr. The cooled mass was cautiously drowned with 100 g of ice; after cooling, the solution was extracted with two 140 ml portions of chloroform (extracts discarded). Cold, concentrated ammonium hydroxide was used to neutralize the acid solution to the phenolphthalein endpoint; external cooling was required. The separated salts were removed on a large fritted glass funnel. This solid cake was carefully slurried in the funnel with 350 ml of diethyl ether; the ether was then drawn off and used to extract the aqueous phase. This procedure was repeated three more times. The combined extracts were dried over anhydrous potassium carbonate, filtered, and evaporated to leave an orange colored, mushy solid; 46.7 g (70%). The crude product was slurried with 50 ml of diethyl ether, chilled to $0\,^\circ$C, filtered through a cold funnel, washed once with cold ether and dried, 35.2 g (53%). Further purification can be effected by several recrystallizations from n-hexane (about 12 g of compound can be recovered per 500 ml of solvent); off-white or pinkish plates: nmr ($CCl_4$) $\tau$ 7.22 (t, 4, $J = 7.5$ Hz, $H_4$, $H_4'$), 6.14 (t, 4, $J = 7.5$ Hz, $H_3$, $H_3'$), 2.75 (m, 8, $H_{aromatic}$).

#### 3.2. 3,3′,4,4′-TETRAHYDRO–1,1′-BIISOQUINOLINE AND METHYL IODIDE

Tetrahydro–biisoquinoline, **5**, (2.6 g, 0.001 mole) in 10 ml of dry acetonitrile was treated with 3.3 g (0.023 mole) of methyl iodide. The slightly exothermic reaction soon deposited much fine yellow solid; upon standing overnight at ambient temperature recrystallization had converted the solid to large orange crystals. (If allowed to stand at ambient for 5 days, some

## TABLE 3

### 3,3',4,4'-Tetrahydro-1,1'-biisoquinoline derivatives

| Derivative | Formula | mp (°C) | Recry. solvent | Calculated (%) C | H | N | X[a] | Found (%) C | H | N | X[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Parent (5) | $C_{18}H_{16}N_2$ | 105–106[b] | n-Hexane | 83.04 | 6.13 | 10.76 | | 83.24 | 6.27 | 10.70 | |
| Parent (5), dipicrate | $C_{30}H_{22}N_8O_{14}$ | 145–146 | Abs. ethanol | | | 6.50 | 37.06 | | | 6.34 | 37.02 |
| Parent (5), dihydrobromide | $C_{18}H_{18}N_2Br_2 \cdot 0.5H_2O$ | 235–240 (dec) | Ethanol + ether | | | | | | | | |
| 2-Methyl-, iodide[c] | $C_{19}H_{19}N_2I$ | 207–208 (dec) | 95% Ethanol | 56.72 | 4.76 | 6.97 | 31.55 | 56.86 | 4.78 | 6.91 | 32.94 |
| 2-Methyl-, dipicrate | $C_{31}H_{24}N_8O_{14}$ | 128–129 | Abs. ethanol | 50.82 | 3.30 | 15.30 | | 50.86 | 3.46 | 14.97 | |
| 2-Methyl-2'-hydro-, diiodide | $C_{19}H_{20}N_2I_2$ | 210–212 (dec) | 80% Ethanol + ether | 43.04 | 3.80 | 5.28 | 47.88 | 43.04 | 3.70 | 5.16 | 48.01 |
| 2,2'-Dimethyl-, diiodide (1) | $C_{20}H_{22}N_2I_2$ | 214–216 (dec) | 80% Ethanol | 44.13 | 4.08 | 5.15 | 46.64 | 44.03 | 4.20 | 5.10 | 46.63 |
| 2,2'-Dimethyl-, diperchlorate | $C_{20}H_{22}N_2Cl_2O_8$ | 190–192 (dec) | Abs. ethanol | | | 5.73 | 14.49 | | | 5.77 | 14.35 |
| 2-Ethyl-, iodide | $C_{20}H_{21}N_2I$ | 203–205 (dec) | 2-Propanol | | | 6.73 | 30.49 | | | 6.61 | 30.67 |
| 2,2'-Diethyl-, diiodide[d] | $C_{22}H_{26}N_2I_2 \cdot H_2O$ | 205–206 (dec) | 80% Ethanol | 44.76 | 4.78 | 4.75 | 43.00 | 45.00 | 4.51 | 4.78 | 43.04 |
| 2-Benzyl-, bromide | $C_{25}H_{23}N_2Br$ | 169–171 | 2-Propanol | 69.61 | 5.37 | 6.49 | 18.52 | 69.57 | 5.63 | 6.45 | 18.53 |

a X = halogen.

b Matsuo et al.[19] reported 76°C.

c This salt dissolves in CHCl3; a saturated solution soon deposits pale yellow felted needles of a solvate.

d When recrystallized from 80% ethanol, this salt was obtained as orange needles, probably a solvate; vacuum drying at 80°C, 25 mm, converted it to a dark red powder.

conversion to the dark red-purple dimethiodide was noted; but even after 3 months, the conversion was still not complete.) The yield of mono-methiodide was 3.9 g (97%); mp 203–204 °C. The sample for analysis was recrystallized from 95% ethanol and vacuum dried at 68 °C, 20 mm, for 24 hr; analyses are listed in table 3; nmr (DMSO-$d_6$) $\tau$ 6.27 (s, 3, –NCH$_3$), 6.87 (t, 2, $J = 7.5$ Hz, H$'_4$); 6.51 (doubled triplet, 2, $J_t = 7.0$ Hz, $J_d = 6.0$ Hz, H$_4$); 5.89 (doubled triplet, 2, $J_t = 7.5$ Hz, $J_d = 3.5$ Hz, H$'_3$); 5.54 (t, 2, $J = 8.0$ Hz, H$_3$); 2.1–2.7 (m, 8, H$_{aromatic}$).

A dark red hydroiodide was prepared by dissolving some of the above monomethiodide in 80% ethanol, adding excess 48% hydroiodic acid, and precipitating with diethyl ether. The $^1$H nmr spectrum was essentially the same as the previous one except for an additional singlet at $\tau$ 1.5 (1 H).

When 0.02 mole of 5 and 8 ml of methyl iodide were refluxed in 100 ml of acetonitrile under a 0 °C condenser for 18 hr, much dark red solid crystallized. After the solution had been chilled to 5 °C, the dimethiodide was removed; 5.7 g (52%). The dark, red-purple blades obtained upon recrystallization from 110 ml of 80% ethanol were dried at 72 °C, 25 mm; nmr (DMSO-$d_6$) $\tau$ 6.04 (s, 6, –NCH$_3$), 6.32 (t, 4, $J = 7.5$ Hz, H$_4$, H$'_4$), 5.30 (t, 4, $J = 7.5$ Hz, H$_3$, H$'_3$), complex multiplet centered at 2.32 (8, H$_{aromatic}$).

### 3.3. 3,3′,4,4′-TETRAHYDRO-1,1′-BIISOQUINOLINE AND ETHYLENE DIBROMIDE

Two grams of 5 and 15 ml of ethylene dibromide were refluxed for 2 hr under air. When the cooled solution was treated with a large excess of acetone there was recovered 3.46 g of dark solid, mp 140–150 °C. The latter was dissolved in 30 ml of ethanol plus 280 ml of acetone and treated with 350 ml of ether; 1.14 g of brown solid, decomposing 250–280 °C, precipitated. This solid was further purified by dissolving in 15 ml of water and fractionally precipitating with acetone (the initial, black tarry fractions were discarded.) Finally, an orange-brown crystalline product, mp 280–290 °C, was obtained; its $^1$H nmr spectrum in D$_2$O was the same as that of authentic 2.

*Anal.* Calculated for C$_{20}$H$_{16}$N$_2$Br $\cdot$ 2H$_2$O: C, 51.97; H, 3.92; N, 6.06; Br, 34.58. Found: C, 51.86; H, 3.84; N, 6.03; Br, 34.57.

Conversion to the perchlorate and recrystallization from water gave a yellow salt melting above 310 °C.

*Anal.* Calculated for C$_{20}$H$_{16}$N$_2$Cl$_2$O$_8$: N, 5.80; Cl, 14.68. Found: N, 5.76, 5.49; Cl, 14.58, 14.75.

The original alcohol–acetone-ether mother liquors were evaporated to leave a hygroscopic, brown resin. Solution in dry acetonitrile and fractional precipitation with diethyl ether finally gave a tan solid decomposing above 300 °C. The poorly soluble, orange-brown perchlorate, made from the

bromide and sodium perchlorate in water, decomposed 245–250 °C after recrystallization from 95 % ethanol. The $^1$H nmr results on the perchlorate and analyses on the bromide are consistent with those required for a 1,2-bis(3,3′,4,4′-tetrahydro-1,1′-biisoquinolyl-2)ethane salt: nmr (DMSO-$d_6$) $\tau$ 6.85 (t, 8, $J$ = 6.0 Hz, H$_4$, H$_4'$), broad unresolved multiplet centered at 6.42 (4, ethylene bridge), 5.75 (t, 8, $J$ = 6 Hz, H$_3$, H$_3'$), 2.58 (m, 12, H$_{aromatic}$), 2.20 (m, 4, H$_{aromatic}$).

*Anal.* Calculated for $C_{38}H_{36}N_4Br_2$: C, 64.41; H, 5.12; N, 7.91; Br, 22.56. Found: C, 64.52; H, 5.05; N, 7.35, 7.98; Br, 21.94, 22.59.

### 3.4. OXIDATION PRODUCTS FROM 1

The dimethiodide **1** (1.075 g, 0.00198 mole) in 500 ml of de-aerated absolute methanol was treated with 0.44 g (0.008 mole) of sodium methoxide under nitrogen. The orange colored solution became very dark, then rapidly returned to an orange-red color. This solution was then oxidized with dry air for 6 hr; the color gradually changed to pale yellow. The still basic solution was adjusted to the phenolphthalein end-point with hydrochloric acid, and evaporated to dryness at room temperature. The gummy residue was extracted several times with ether, and the combined extracts evaporated to leave 0.66 g of amber oil. The oil was chromatographed on a $\frac{1}{4}$ in. × 10 in. Al column, packed with 20 % SE-52 Chromosorb-W (AWDMCS), 60 ml, He/mm, 190 °C column temperature. Four principal fractions were collected (retention times: 6, 19, 22, and 26.5 min) although trace amounts of at least three other constituents were noted. Peak areas were integrated. The last three fractions had strong carbonyl absorptions at 6.1 μm; structure assignments were made on the basis of mass spectra. The results can be summarized as follows:

3,4-Dihydroisoquinoline, 3.1 %, $m/e$ = 131 (parent), 103 (M–$C_2H_4$).

2-Methyl-3,4-dihydroisoquinolone-1, 50.0 %, $m/e$ = 161 (parent), 118, 90.

2-Methylisoquinolone-1, 9.2 %, $m/e$ = 159 (parent), 130, 118.

2-Methoxymethylene-3,4-dihydroisoquinolone-1, 37.8 %, $m/e$ = 191 (parent), 176 (M–$CH_3$), 160 (M–$OCH_3$), 148, 130, 118, 105, 103, 90, 77, 45, 42; a precise mass determination on $m/e$ = 176 indicated $C_{10}H_{10}NO_2$, one at $m/e$ = 130 indicated $C_9H_8N$; nmr (CDCl$_3$) $\tau$ 6.73 (s, 3, –OCH$_3$), 7.08 (t, 2, $J$ = 6.5 Hz, H$_4$), 6.45 (t, 2, $J$ = 6.5 Hz, H$_3$), 5.13 (s, 2, CH$_2$ between N and O), 2.82 (m, 3, H$_5$, H$_6$, H$_7$), 2.12 (m, 1, H$_8$).

The ether insoluble residue was extracted several times with warm 2-propanol (an aqueous solution of the insoluble salts still had yellow-green fluorescence) and the extracts evaporated. This solid residue was dissolved in 15 ml of 80:20 benzene:absolute ethanol, treated with 20 ml of benzene, and chilled to 5 °C; more sodium iodide separated and was removed.

Evaporation of the benzene solution left 0.23 g of pale yellow, amorphous solid, which had a strong carbonyl absorption at 6.1 μm and which was soluble in water or alcohol; these solutions had a yellow-green fluorescence. An attempt to fractionate a 2-propanol solution by incremental addition of ether gave cuts melting at 180–181 °C (in MeOH, fluorescence peaked at 385 nm), 158–160 °C, 130–140 °C, and 120–125 °C (sample used to obtain spectrum in fig. 6). All were still amorphous in appearance. A mass spectrum on the second fraction showed a parent ion of 362 which suggests retention of the biisoquinoline structure (other peaks occurred at $m/e = 161, 147, 118, 90$); the mass spectrum on the last fraction was very similar.

In another experiment, 0.5 g of 1 was dissolved in 50 ml of 50 % aqueous methanol and made basic with sodium hydroxide solution. The orange-red solid which separated was extracted into ether; the etheral solution was washed twice with cold water, dried over sodium sulfate, then evaporated. Upon standing overnight exposed to the air, the orange-red gummy solid changed to an amber oil which was now only partially soluble in ether (the insoluble was similar to the yellow amorphous solid isolated above). The ether–soluble (0.3 g) fraction contained the same four main oxidation products; however, the ratio of 2-methyl–3,4-dihydroisoquinolone-1 to the methoxy derivative was 3:1 instead of the 5:4 observed above.

Separation of the ether–soluble, oxidation products by TLC (Mallinkrodt Silicar TLC-7GF on glass plates; ethyl acetate–n-hexane, 1:1, for development) revealed the same fractions. The phosphor in 7GF was quenched by the three carbonyl compounds; none of them was sufficiently concentrated on the plate to show by its own fluorescence. Since separation of two of the fractions were better by TLC than glc, preparative TLC was employed to get samples for fluorescence measurements; the proper section was removed from the plate, slurried with 3 ml of methanol, and the absorbent separated by centrifuging.

### 3.5. SPECTRAL MEASUREMENTS

All emission and most absorption spectra were run on the Turner Spectro-fluorometer[12]). This instrument mechanically corrects the emission spectra for the spectral sensitivity of the photomultiplier and emission monochromator. Thus, equal radiant flux per wavelength unit gives equal heights at all wavelengths[18]). Our spectra are taken directly from the instrument.

Chemiluminescent spectra were run in 1 cm square cuvettes. A flow system mixed oxygen saturated streams of liquid just above the flow cell in the instrument. Static runs were of two types. The biisoquinolinium salt and base could be mixed within the cuvette in air to start the reaction. Alternatively, the reactants were mixed under $N_2$ and the reaction started by

removing the Teflon stopper from the cuvette. The light versus time curves were taken by adding $O_2$ to stirred basic solutions in an apparatus described previously[13]).

## Acknowledgment

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# CHEMILUMINESCENCE: QUANTUM YIELDS FOR
# LUMINOL AND A BIISOQUINOLINIUM SALT

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Quantum yields of chemiluminescence have been measured using a relatively simple technique involving a black reaction vessel, a black box, and a spectrally calibrated photomultiplier. The mathematical solutions of the geometric and spectral equations are presented and discussed. The specific chemical conditions used for luminol and a bi-isoquinolinium salt are described. These gave quantum yields of 0.81% and 0.48%, respectively, for luminol and the BIQ salt.

## 1. Introduction

As stated in refs. 1 and 2, the measurement of quantum yields and light output from chemiluminescent reactions is difficult but important. The yields for luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) reported[1-3] differ by a factor of 4. In general, there are few reports of close agreement between results on identical reactions from different laboratories. The present paper presents absolute quantum yields for two reactions which have been previously reported. The biisoquinolinium (BIQ) salt was called I by Mason and Roberts[4]) and is 8,9-dihydropyrazino-[1,2-a:3,4-a'][1,1']-biisoquinolinium dibromide monohydrate. Our methods are different from the others and, we think, more easily adopted by other laboratories.

## 2. Photometry

The principle of these absolute measurements is to have a relatively small, liquid source illuminating a spectrally calibrated photodetector from a large distance. The source is in a black vessel with no transparent glass to trap or to pipe light. Then there is little error in assuming the source an infinitesimal volume and the detector an infinitesimal area on an illuminated sphere[5]). The total light radiated can be calculated if the dimensions and the optical properties of the system are known and the irradiance of this one area is measured. For ease of calculation, we have placed the detector directly above the center of the liquid filled vessel.

In this case, the total light from a run is given by

$$Q = \frac{1}{1+r}\,\frac{1}{t}\,\frac{1}{g}\,\frac{1}{S}\int R\,dt. \tag{1}$$

Here: $r$ = reflectivity of vessel bottom, $t$ = transmission of any intermediate windows, $g$ = geometric factors, $S$ = effective sensitivity of detector and $\int R\,dt$ is the area under the reaction-emission curve. The geometric factor, $g^{-1} = 4\pi h(h-d)\eta^2$, where $h$ is the distance from vessel bottom to detector surface, $d$ is the liquid depth, and $\eta$ is the index of refraction of the solution. The term $h(h-d)$, the first term of an expansion series, is a good approximation if $d \ll h$. The true illuminance above a circular emitting surface is inversely proportional to $(h^2 + \rho^2)$ where $\rho$ is the radius of the circle. If $\rho \leq 0.1\,h$, the error in using $h^2$ is less than 1%. Thus, the factors $h(h-d)$ will be a good approximation in a large box with relatively small reaction vessels and shallow liquid samples. The index of refraction term accounts for the spreading effect on a cone of light passing out of a liquid. For dilute solutions, the solvents $\eta$ may be used.

The effective sensitivity of the photodetector for light from a particular chemiluminescent reaction, $i$, is given by:

$$S_i = S_m \frac{\int f_i s_\lambda\,d\lambda}{\int f_i\,d\lambda} = S_m\,F_i. \tag{2}$$
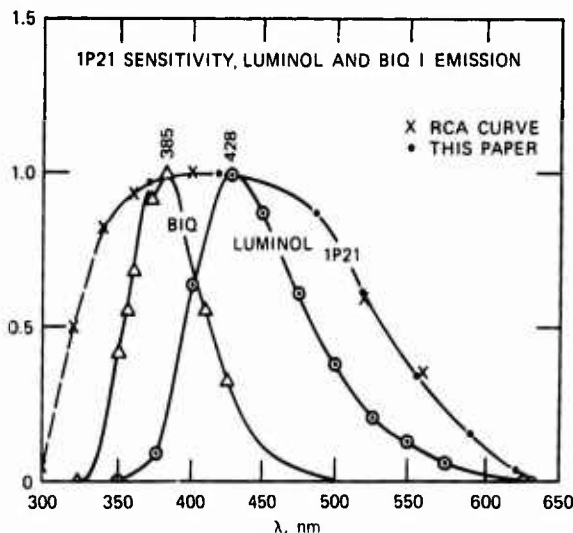


Fig. 1. Sensitivity and emission spectra. These normalized spectra are used in the calculation of $S_i$ and $F_i$. The shape of the normalized measured sensitivity curve (s) is very close to that published by RCA for the S4 response of 1P21 photomultiplier tubes. (●) Our points; (×) RCA curve.

Here $S_m$ is the maximum sensitivity (fig. 1), while $f_i$ and $s_\lambda$ are the normalized spectral curves for the chemiluminescent emission and the detector sensitivity. $F_i$ is an effectivity factor and is 0.894 for luminol and 0.986 for BIQ I. The maximum sensitivity varies with time, but the spectral sensitivity curve was nearly constant.

## 3. Apparatus

The detector was an RCA 1P21 photomultiplier tube and a Photovolt Model 520-M photometer. A Moseley high impedance recorder was attached directly across the dial (1000 ohm) of the photometer. There was one window on the detector and this was left on during calibration and runs.

Calibration was done with an NBS calibrated tungsten strip lamp run at 35 A using an EG and G power supply Model 590-11A. Narrow bandpass filters from Optics Technology were used for isolating particular wavelength regions. The calculation of illuminance required painstaking calculation of the filter and emission curves. Actually, the sensitivity curve for our 1P21 tube essentially matched the normalized curve for an S-4 response published by RCA[6]) and we need only have measured $S_m$ at 400 mm. Fig. 1 shows the spectral sensitivity which is very close to the published[6]) S-4 response. The sensitivity at the peak, $S_m$, during the luminol runs was $8 \times 10^{20}$ mV $\cdot$ einstein$^{-1} \cdot$ sec $\cdot$ mm$^2$. This had changed to $4.4 \times 10^{20}$ during the BIQ runs. Calibrations were made before and after each series of absolute quantum yield runs.

The emission spectra of the chemiluminescers were measured on a Turner Model 210 Spectro Fluorometer and are automatically corrected for spectral sensitivity in terms of einstein/wavelength interval. The luminol spectra were taken for the slow reaction using $H_2O_2$ and $K_2S_2O_8$ as co-catalysts[7]). These spectra match those reported elsewhere[8]) for the luminol reaction in water solution.

The BIQ runs were taken using a flow system. The spectrum shifted somewhat (to 425 nm) during a run, but was as shown in fig. 1 for most of the reaction period.

The chemiluminescent reactions were run in blackened vessels of various types. Thus, each volume element of the glowing liquid illuminates the detector directly, but in no other way. Using clear glass cylinders or pyrex beakers, we always obtained higher light readings due to reflections and light piping. To avoid light piping to the rim of our 15 ml, black painted beakers, we frosted the exteriors before painting them. Bakelite caps with the inserts removed made good vessels. A 31 mm ID, black nylon vessel was especially machined for this use. Using these different vessels we ob-

tained nearly equal results by assuming reflectivity as zero for all of them.

There are three other sources of small errors in connection with the vessels. Some light will be reflected back at the liquid–air interface and we have not corrected for this effect which should be less than 3%. Near the vessel's walls the liquid meniscus will distort the light path, probably in a manner to decrease $Q$. Finally, stirring might distort the optical qualities of the liquid surface. However, experiments showed no change in measured light with stirring and that actually we did not need to stir our solutions.

The general procedure was to place our vessel in a black box with an external magnetic stirrer. One solution was placed in the vessel and the box closed. The photomultiplier was turned on and the second solution added to the vessel through a long stainless steel needle from outside the box. Thus, we were able to detect and record all the light.

To premix BIQ and NaOCH$_3$ under N$_2$ we used an N$_2$ box from the Vacuum-Atmospheres Company of Los Angeles. An antechamber was fitted with a window for viewing the vessel filled with the solution. Reaction was initiated by pumping out some N$_2$ and replacing it with air. Photometric measurements were corrected for the transmittance of the windows. Stirring again showed no effect on the amount of light measured.

The dimensions of the wooden black box gave $h = 228.7$ mm, while the liquid depth was never more than 3.1 mm. In the antechamber, $h = 275$ mm and $d = 1$ mm.

The light output was recorded as the area under a pen drawn curve and measured in mV · min. Eq. (1) was used to calculate $Q$, the output in einstein. The quantum yield $q = Q/n$, where $n$ is the number of moles of luminol or BIQ I.

## 4. Material

Luminol was purchased from Aldrich Chemical Company and purified by a special recrystallization[9]) and by sublimation at 220–230 °C at 0.5 torr. Several samples of unpurified and doubly or triply repurified luminol were tested for relative light output. The original material* was as good as any purified samples.

Luminol solutions[1, 3]) were made up in 0.1 N NaOH using about 20 mg per liter which gives 112.9 μM. There is an absorption band peaking near 348 nm where $\varepsilon = 7000$ M$^{-1}$. Stored in polyethylene, these solutions weakened slightly on standing in light. The stock luminol solutions were

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* Not all manufacturers' samples were equally good and one batch gave no visible light.

usually used in a 1:10 dilution with buffer solution although a few runs were made undiluted.

The buffer solution was made using 1.417 g of $Na_2HPO_4$ and 15 g of $Na_3PO_4$ per liter. Its pH tested as 11.8.

The Eastman–Kodak hemin was used as received. A stock solution was made using 10 mg in 250 ml of the phosphate buffer solution. This solution was 6.12 µM based upon the stated molecular weight of 651.95. The molar absorbance at the 385 nm peak was $\varepsilon = 32.2 \times 10^3$ $M^{-1}$. At the 350 nm shoulder $\varepsilon = 29.1 \times 10^3$ $M^{-1}$. These absorbances and peaks differ somewhat from those reported earlier[1]). The hemin solutions were stored at 5 °C.

Hydrogen peroxide of 0.1 % concentration was made by diluting 0.33 ml of 30% B & A code 1802 $H_2O_2$ to 100 ml with distilled water. This was made freshly each day.

The average barometer pressure is 700 torr so that $O_2$ quenching is presumably slightly less than at sea level.

Thus, our chemical conditions were as close as possible to those described earlier[1]) with the hemin the only chemical difference. The physical-optical technique was quite different.

The BIQ I was prepared by a method of Mason and Roberts[10]). It has a molecular weight of 462.190, darkening 270–280 °C, but not melting up to 300 °C. Solutions of about $5 \times 10^{-4}$ M in methanol were prepared. Under air these were yellow with an absorption peak at 345 nm ($\varepsilon = 6192$ $M^{-1}$). We also prepared solutions under $N_2$ which were $5 \times 10^{-4}$ M in BIQ I and 0.1 M in $NaOCH_3$. These turn an orange-red color due to absorption of the olefins formed from the dication. These solutions have absorption peaks at 500 and 538 nm – actually a broad band from 470–570 nm at half peak height.

## 5. Procedures

With luminol we added first 1 ml of the diluted luminol solution. Then 0.1 ml of $H_2O_2$ was added which gave a small but variable peak of light. Presumably, the amount depended upon impurities in the beaker and syringes. The area of this peak was included in the total light, but was never more than a few percent of the total.

Hemin was added either full strength or as a 1:3 dilution in 0.1 ml volumes. Succeeding additions of hemin gave smaller peaks of light. With stock solution two 0.1 ml "shots" containing about 1.2 nanomoles of hemin exhausted the initial 11.29 nanomoles of luminol.

The BIQ I solutions were mixed with aqueous NaOH under the detector. The procedure was to place the NaOH solution in the vessel, close the black

box and turn on the detector. BIQ solution was added through a small hole in the box using a 4 inch needle and a syringe. The light production was very rapid at 25 °C with 90 % of the light produced within 10 sec.

The premixed solutions of BIQ I and $NaOCH_3$ were measured into a black vessel and placed in the windowed antechamber. Part of the $N_2$ was evacuated and replaced with air to produce the oxy-luminescence. These reactions were slower than the others since oxygen had to diffuse to the solution.

## 6. Results and discussion

The absolute quantum yields are shown in tables 1 and 2. For luminol we get values close to but lower than the $1.14 \pm 0.06 \%$ under air reported by Lee et al.[1]) and by Lee and Seliger[3]). Our value of $0.81 \pm 0.05 \%$ is much larger than the value of Hastings and Reynolds[2]). We cannot be certain about which values are better, but it is possible to analyze for some errors in our method and in Lee's method.

When we used a method similar to that described[3]) by the earlier workers our values for BIQ were higher. We ascribed this to light piping and re-

TABLE 1

Quantum yield of luminol

| Luminol | Solution | Vessel | $q$ (%) | $\sigma$ (%) |
|---------|----------|--------|---------|--------------|
| Aldrich | Freshly prepared | Black painted beaker | 0.824 | 0.038 |
| Aldrich | 1 week old | Black painted beaker | 0.818 | 0.020 |
| Aldrich | 1 week old | Brown glass vessel | 0.780 | 0.050 |
| Recrystallized | Freshly prepared | Black painted beaker | 0.826 | 0.036 |

$T = 25 \pm 1 °C$, 700 torr air pressure;
1.03 ml luminol, 112.9 $\mu M$;
0.1 ml $H_2O_2$, 1 %;
0.1 ml portions of hemin, see text;
detector: $S_{max} = 7.96 \, (\pm 0.11) \times 10^{20} \, mV \cdot einstein^{-1} \cdot sec \cdot mm^2$

flectance from the liquid in a clear glass cuvette. It was for this reason that we changed to blackened vessels with only the one liquid–air interface close to the emitting source. The runs in the white teflon vessel show how much more light is directed vertically by a lambert surface. Calculations show it could approach four times as much while specular reflection can only approach twice as much as a totally black vessel.

Physical sources for error include detector calibration and the negative

TABLE 2

Quantum yields of BIQ I

*Methanol solution, premixed under $N_2$; air added*

| [BIQ I] (mM) | [NaOCH₃] (M) | Volume (ml) | q (%) | σ (%) |
|---|---|---|---|---|
| 0.50 | 0.1 | 1 | 0.48 | 0.05 |

*Mixed in air; NaOH in water; BIQ I in methanol*

| [NaOH] (M) | Volume (ml) | [BIQ I] (mM) | Volume (ml) | Vessel | q (%) | σ (%) |
|---|---|---|---|---|---|---|
| 0.01 | 1 | 0.424 | 2 | Bakelite cap | 0.29 | 0.02 |
| 0.01 | 1 | 0.424 | 1 | White teflon | (0.89) | |
| 0.01 | 1 | 0.424 | 1 | Pyrex painted black | 0.26 | 0.05 |
| 0.01 | 1 | 0.523 | 1 | Black nylon | 0.22 | 0.02 |
| 0.1 | 1 | 0.523 | 1 | Black nylon | 0.30 | 0.03 |

errors if all the light does not leave the solution. Detector calibration in our case depended upon one source – the calibrated lamp and the optical train built by us. In this respect. our results are open to more question than Lee and Seliger's[3]).

It is possible that our luminol solutions gave less light than the hemoglobin catalyzed solutions. This we could not check. The luminol itself seemed quite pure as judged by the results with variously purified and repurified material.

Mason and Roberts[4]) reported a quantum yield of 0.15% for BIQ I compared to 0.30% for lucigenin[11]). Our values are 0.48% for premixed and 0.25% for air mixed solutions. It is well to discuss the possible errors in the BIQ case.

The sensitivity curve is somewhat doubtful below 418 nm as indicated in fig. 1. However, the fit to RCA data above 418 nm gives some confidence for the overall shape in the uv.

The BIQ emission spectra shifts[12]) during a run with the peak moving to 425 from 385 nm. However, the change in $S_i$ is quite small.

The dark color of the cation-radical would not absorb much light around 385 nm, but the dication and products may absorb a little. Some results indicate that this is small. We ran several series in which three to six ml portions of BIQ solution were added successively to a 1 ml portion of 0.1 N NaOH. Each portion gave equal light. Thus, the depth of absorbing solution had small effect. This also shows that the products do not "quench" the light-producing reactions nor excited species at these concentrations.

The larger quantum yield for premixed BIQ solutions is not due to the lower $O_2$ concentration. 700 torr of $O_2$ only gives 10% quenching of either chemiluminescence or of the fluorescence of the product isoquinolones[12]).

## Acknowledgements

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5)  F. W. Sears, *Principles of Physics*, Vol. III, Optics (Addison-Wesley, 1948) ch. 13
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# Reactions of Epimeric 2,2'-Diacetyl-1,1',2,2'-tetrahydro-1,1'-biisoquinolines

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The title compounds are brominated by NBS to yield epimeric 2,2'-diacetyl-4,4'-dibromo-1,1',2,2'-tetrahydro-1,1'-biisoquinolines rather than 1,1'-dibromo derivatives as reported previously. Cleavage of the 1,1' bond characterizes attempts to aromatize these compounds by oxidative methods; e.g., the dibromo derivatives are converted to 4-bromoisoquinoline in 90% yield by 5.3 N nitric acid at 30°. dl- and meso-4,4'-dibenzal-1,1',4,4'-tetrahydro-1,1'-biisoquinolines are recovered in low yields when the title compounds are heated in ethanol with benzaldehyde and concentrated hydrochloric acid; extensive cleavage of the 1,1' bond again occurs with the formation of 4-benzal-1,4- (and 3,4-) dihydroisoquinoline. 5,5'-Dinitro- and 5-nitro-1,1'-biisoquinoline are described.

Previously it was reported[1] that both epimers of 2,2'-diacetyl-1,1',2,2'-tetrahydro-1,1'-biisoquinoline (**1a,b**)



**1a**, *dl*
**b**, meso



**2a**, *dl*
**b**, meso
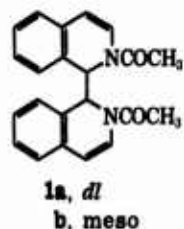


(prepared by the Dimroth reaction from isoquinoline, zinc, and acetic anhydride) and *N*-bromosuccinimide reacted in acetic acid to give epimeric dibromo compounds, $C_{22}H_{18}Br_2N_2O_2$. Alkaline hydrolysis of the latter gave mixtures of isoquinoline and a bromoisoquinoline (approximately equimolar). Based in part on the melting point of the bromoisoquinoline recovered by preparative glc, this compound was considered to be the 1-bromo isomer; the dibromo compounds were then considered to be epimeric 2,2'-diacetyl-1,1'-dibromo-1,1',2,2'-tetrahydro-1,1'-biisoquinolines.

Subsequent work (mixture melting points, comparison of ir spectra, ^{1}H nmr) has shown that this bromoisoquinoline is actually the 4 isomer. Consequently, the dibromo compounds are reformulated as 2,2'-diacetyl-4,4'-dibromo-1,1',2,2'-tetrahydro-1,1'-biisoquinolines (**2a,b**). This assignment is confirmed by the proton nmr spectrum[2] on the lower melting, more-soluble, *dl* isomer, **2a**.

Cleavage of the 1,1' bond with formation of a mixture of isoquinoline and 4-bromoisoquinoline is also observed
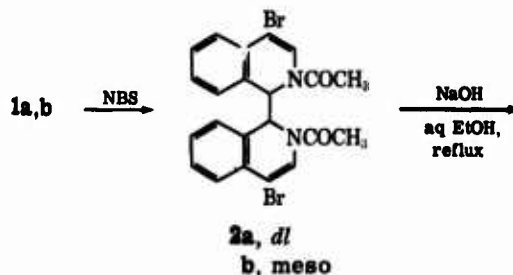
when **2a** and **2b** are oxidized by refluxing nitrobenzene. On the other hand, oxidation of **2a** with 5.3 N nitric acid at 30° gives 4-bromoisoquinoline in 90% yield.

Aromatization of **2a** without cleavage of the 1,1' bond so as to recover 4,4'-dibromo-1,1'-biisoquinoline was attempted by the procedure of Knabe.[3] The latter had demonstrated that laudanosine could be oxidized to *N*-methylpapaverinium and *N*-methyl-3,4-dihydropapaverinium salts by mercuric acetate and disodium ethylenediaminetetracetate in aqueous acetic acid; other oxidation conditions had caused cleavage at the 1-methylene bond. However, even after prolonged heating at 80–85° only partial oxidation of **2a** had occurred; small amounts (<15%) of impure 4-bromoisoquinoline were isolated, suggesting that cleavage was still the preferred route.

The conversion of **1a,b** directly to 1,1'-biisoquinoline or derivatives has been further investigated beyond the results reported previously.[1] Extensive cleavage of the 1,1' bond again characterizes most of the reactions.

(1) A. T. Nielsen, *J. Org. Chem.*, **35**, 2498 (1970).

(2) ^{1}H nmr for *dl*-2,2'-diacetyl-4,4'-dibromo-1,1',2,2'-tetrahydro-1,1'-biisoquinoline: τ (CDCl₃) 2.42 (dd, 1, $J = 7.5$, 1.5 Hz, H₅), 2.69 (td, 1, $J = 7.5$, 1.5 Hz, H₆), 2.94 (s, 1, H₃), 3.15 (td, 1, $J = 7.5$, 1.5 Hz, H₇), 4.02 (dd, 1, $J = 7.5$, 1.5 Hz, H₈), 4.15 (s, 1, H₁), 7.83 (s, 3, COCH₃).

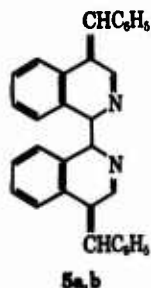(3) J. Knabe, *Arch. Pharm. (Weinheim)*, **292**, 416 (1959).

For example, isoquinoline (IQ) is formed from **1a** at room temperature with chloranil in aqueous acetic acid, with activated manganese dioxide in acetonitrile, and with cupric chloride in acetonitrile (the 1:1 complex, CuCl₂-IQ, precipitates). Oxidation of **1b** with either 5.3 N or 8 N nitric acid proceeds rapidly and exothermically at room temperature; isoquinoline is recovered in 90-95% yield. Nitration of **1a** in concentrated sulfuric acid at 3-7° furnishes 5-nitro- and 4,6-dinitroisoquinoline. Under the same conditions of nitration, 1,1'-biisoquinoline was converted to 5,5'-dinitro- and 5'-nitro-1,1'-biisoquinoline (73 and 21%, respectively).

3,3'-Biisoquinoline was isolated in low yield from **1b** by refluxing in nitrobenzene with 10% palladium/charcoal catalyst; the principal product was isoquinoline. In the absence of Pd/C, no biisoquinoline was formed. It has been suggested by Carey and Sasse[4] that 3,3'-biisoquinoline is formed with 1,1'- and 1,3'-biisoquinolines when isoquinoline is heated with rhodium/carbon catalyst.

Since there is substantial evidence[5,6] that 1,2-dihydroisoquinolines are intermediates in the synthesis of 4-benzylisoquinolines from benzylaminoacetaldehyde dialkyl acetals, aromatic aldehyde and acid, the reaction of the 1,2-dihydroisoquinoline derivatives, **1a,b**, with benzaldehyde and hydrochloric acid was examined. A variety of products were formed; the principal one, which again arose from a cleavage of the 1,1' bond, was a mixture (based on the nmr spectrum) of **3** and **4**.
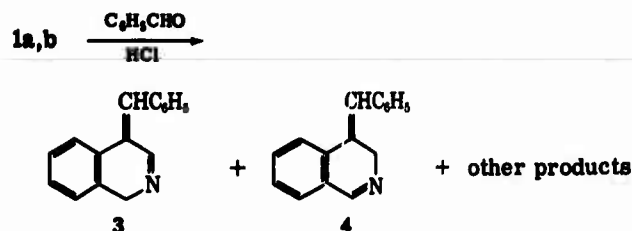


Similar isomers have been found previously in this type of reaction.[6] More importantly, two other high-melting isomers were recovered in low yield; their molecular weights and mass spectral behavior indicated that they were derivatives of 1,1'-biisoquinoline. Because the ¹H nmr spectra showed methine but no benzyl methylene protons, the compounds are considered to be epimers **5a,b**. Other compounds, including some isoquinoline,



were also isolated in low yield as their picrates, but were not characterized by nmr.

## Experimental Section

**Oxidation of 2a,b with Nitrobenzene. A.**—The meso isomer (**2b**)[1] (4.0 g) was refluxed for 3 hr with 40 ml of nitrobenzene; the poorly soluble amide gradually dissolved to give a yellow solution which turned red, then dark brown. The cooled solution after dilution with 50 ml of 95% ethanol and 200 ml of diethyl ether was extracted with one 80 ml and one 25 ml portion of 3 N hydrochloric acid. The combined acid solutions were reextracted with 100 ml of fresh ether (discarded), made basic, and extracted with three 70-ml portions of ether. After drying over anhydrous potassium carbonate, the ether solution was evaporated to leave 2.5 g of red liquid. An analytical glc showed 12.0, 41.0, and 42.7 mol %, respectively, of nitrobenzene, isoquinoline, and 4-bromoisoquinoline (samples of the last two compounds, isolated by preparative glc, had ir spectra identical with those of authentic specimens): ¹H nmr for 4-bromoisoquinoline τ (CDCl₃) 0.85 (s, 1, H₁), 1.28 (s, 1, H₃), 1.7-2.5 (m, 4, H₅, H₆, H₇, H₈).

**B.**—A similar experiment with the dl isomer (**2a**) gave 2.66 g of product which contained 27.5 and 66.2 mol %, respectively, of isoquinoline and 4-bromoisoquinoline.

**Oxidation of 2a with Nitric Acid.**—**2a**[1] (1.5 g) was added with stirring to 30 ml of 5.3 N nitric acid at 29°. The temperature rose during 5 min to 31° and held for about 15 min; some oxides of nitrogen were evolved. Stirring was continued at 29° for 3.5 hr. Although the solid never dissolved completely, its character changed. After diluting with 10 ml of water and cooling to −15°, the solid was filtered, washed twice with 2-3 ml of cold water and dried, 1.36 g (84%). [From the mother liquors and washings after basification there was recovered 0.07 g (5.6%) of solid, mp 40-41°, whose ir spectrum was identical with that of 4-bromoisoquinoline.] Recrystallization of a small portion from dilute nitric acid gave felted, flat needles of 4-bromoisoquinolinium nitrate, mp 172-173° dec.

*Anal.* Calcd for C₉H₇BrN₂O₃: Br, 29.48; N, 10.34. Found: Br, 29.44; N, 10.28.

The balance of the salt in a minimum of cold water was made basic; white plates, mp 42-43°, separated upon cooling. Again the ir spectrum was identical with that for 4-bromoisoquinoline; mixture melting point was undepressed.

**Oxidation of 1b with Nitrobenzene. A. Without Catalyst.**—Refluxing 1.6 g of **1b**[1] with 15 ml of nitrobenzene under nitrogen for 3 hr followed by isolation of basic material in a conventional manner gave 1.13 g (95%) of isoquinoline (ir spectrum same as that of an authentic sample).

When the above reaction was attempted at 120-125° for 8 hr, under nitrogen and with stirring, the starting amide was recovered quantitatively.

**B. With Catalyst.**—A slurry of 2.0 g of **1b**, 1.0 g of 10% Pd/C, and 20 ml of nitrobenzene was flushed well with dry nitrogen, then stirred and heated at 120-130° for 3.5 hr. The cooled solution was diluted with 50 ml of benzene, filtered, and extracted with 50 ml of 2.4 N hydrochloric acid, followed by 25 ml of water. The combined aqueous extracts were reextracted once with benzene, made basic with concentrated ammonium hydroxide, and chilled overnight at 5°. The solid which separated was filtered, washed with water and dried, 0.4 g (27%). After two recrystallizations from cyclohexane-benzene (6:4) the melting point was 198-199°; the ir spectrum was the same as that for authentic 3,3'-biisoquinoline,[7] mp 197-198°.

*Anal.* Calcd for C₁₈H₁₂N₂: C, 84.35; H, 4.72; N, 10.93; mol wt, 256. Found: C, 84.51; H, 4.71; N, 10.87; mol wt (vpo), 250.

From the basic aqueous mother liquors remaining after removal of the above solid product, there was isolated through ether extraction 0.91 g (61%) of isoquinoline (ir spectrum) and a few crystals of acetanilide, mp 113-116° (ir spectrum).

Formation of the 3,3'-biisoquinoline in this catalyzed oxidation was not reproducible; in many experiments only a trace or none of this compound was found. Cleavage to isoquinoline was consistently 65-70% under these same conditions; at 100-102° the yield of isoquinoline was only 9% after 6 hr; at 130-140° after 4 hr, it was 85%.

(4) J. C. Carey and W. H. F. Sasse, *Aust. J. Chem.*, **21**, 207 (1968). Compare, however, H. Rapoport, R. Iwamoto, and J. R. Tretter, *J. Org. Chem.*, **25**, 372 (1960), who reported that no biaryl was formed by catalytic dehydrogenation when isoquinoline was refluxed for 24 hr with 5% Pd/C.

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(6) D. W. Brown, S. F. Dyke, and M. Sainbury, *Tetrahedron*, **25**, 101 (1969); S. F. Dyke, M. Sainbury, D. W. Brown, M. N. Palfreyman, and D. W. Wiggins, *ibid.*, **27**, 281 (1971).

(7) F. H. Case, *J. Org. Chem.*, **17**, 471 (1952).

**Oxidation of 1b with Nitric Acid.**—The meso epimer 1b (1.2 g) was slurried with 30 ml of 5.3 N nitric acid at 24°. Within 5 min the temperature had increased to 27° and oxides of nitrogen were being evolved. After 10 more min all of the solid had dissolved (temperature 26°). After standing overnight at 25°, the solution was cooled and made basic with concentrated ammonium hydroxide. Isoquinoline (0.85 g, 93%) separated as a pale yellow oil; the ir spectrum was identical with that for authentic isoquinoline.

With 8 N nitric the reaction was more rapid and exothermic; the yield of isoquinoline was 95%.

**Nitration of 1a.**—Compound 1a[1] (3.44 g; 0.01 mol) was added during 5 min to 30 ml of 96% sulfuric acid at 10–15°. To the resulting slurry was added with stirring 4.5 g (0.044 mol) of powdered potassium nitrate over 1.75 hr while maintaining a temperature of 3–7°. The acetyl compound gradually dissolved, and the color changed from pale orange to dark amber; some frothing occurred. After 1 hr at 5°, the solution was poured over 100 g of ice and made basic with cold, concentrated ammonium hydroxide. The yellow solid was filtered, washed well with cold water and dried, 3.55 g, mp 100–130° (dec).

The crude product was separated into a poorly soluble fraction (1.5 g, mp 165–175°) and a soluble fraction by boiling with 100 ml of 95% ethanol and cooling to 5°. Recrystallization of the former from ethanol gave rosettes melting at 182–183°. The analyses and molecular weight indicate a dinitroisoquinoline.[8] The ^{1}H nmr spectrum is consistent with that required for 4,6-dinitroisoquinoline. This structure was established unequivocally through use of the Eu(fod)$_3$ shift reagent[9] in CDCl$_3$. As expected, the singlet signals assigned to H$_1$ and H$_3$ showed the greatest downfield shift and were broadened. The protons on the benzo ring became well resolved: the signals assigned to H$_5$ shifted the most, since this proton is closest to the heteroatom, and showed only the splitting expected for ortho coupling (9 Hz); H$_7$ showed splitting due to meta coupling (2 Hz), whereas H$_7$, which was shifted the least, appeared as a doublet of doublets (both ortho and meta splitting). If this compound had been the 4,7 isomer, the H$_5$ signal would have again been shifted further downfield than those for the two other benzo protons but would have shown only meta splitting. Signals appeared at $\tau$ (Polysol-d[10]) 1.32 (6-line multiplet, 2, $J_{75}$ = 9 Hz, $J_{65}$ = 2 Hz, H$_6$ and H$_7$), 0.73 (m, 1, $J_{57}$ = 2 Hz plus another 1 Hz splitting, H$_5$), 0.63 (s, 1, H$_1$ or H$_3$), 0.23 (s, 1, H$_3$ or H$_1$).

*Anal.* Calcd for C$_9$H$_5$N$_3$O$_4$: C, 49.32; H, 2.30; N, 19.17; mol wt, 219.15. Found: C, 49.32; H, 2.44; N, 18.93; mol wt (mass spectrum), 219.

From the alcohol soluble fraction, by incremental precipitation with water, there was ultimately recovered 0.9 g of off-white needles melting about 90°. Recrystallization from water gave long felted white needles, obviously hydrated, since they crumbled to a powder when vacuum dried, mp 107–108°. The ir spectrum was identical with that of authentic 5-nitroisoquinoline, whose melting point is reported[11] to be 110°; the ^{1}H nmr spectrum agrees with that expected for the 5-nitro isomer—$\tau$ (CDCl$_3$) 2.12 (t, 1, $J$ = 8 Hz, H$_7$), 1.52 (d, 1, $J_{67}$ = 8.5 Hz, $J_{68}$ = 1 Hz, H$_6$), 1.38 (d, 1, $J$ = 6.5 Hz, H$_4$), 1.27 (d, 1, $J_{78}$ = 8.5 Hz, $J_{68}$ = 1 Hz, H$_8$), 1.08 (d, 1, $J$ = 6.5 Hz, H$_3$), 0.43 (s, 1, H$_1$).

*Anal.* Calcd for C$_9$H$_6$N$_2$O$_2$: C, 62.06; H, 3.47; N, 16.09; mol wt, 174.16. Found: C, 61.82; H, 3.18; N, 16.12; mol wt (mass spectrum), 174.

**Reaction of Benzaldehyde and 1a.**—A crude sample (mp 195–200°) of 1a (3.5 g, 0.01 mol) was refluxed for 6 hr with 4.4 g (0.04 mol) of benzaldehyde, 50 ml of concentrated hydrochloric acid and 50 ml of 95% ethanol. After cooling and diluting with 100 ml of water, the solution was stored overnight at 5°; a small amount of yellow brown gum separated. The supernatant was decanted and saved (see below); the gum was heated with a few ml of ethanol and cooled. The white solid (0.04 g, mp >300°) was filtered and recrystallized from 90% ethanol containing several drops of hydrochloric acid: colorless, coarse

prisms melting at 338–341°. This compound is the dihydrochloride of one of the epimers of 4,4'-dibenzal-1,1',4,4'-tetrahydro-1,1'-biisoquinoline (see below).

*Anal.* Calcd for C$_{33}$H$_{26}$Cl$_2$N$_2$·2H$_2$O: C, 70.45; H, 5.54; Cl, 13.00; N, 5.14. Found: C, 70.63; H, 5.27; Cl, 13.36, 13.07; N, 5.07, 5.17.

The picrate derived from this salt decomposed at 315–318° after recrystallization from ethanol as yellow felted needles.

*Anal.* Calcd for C$_{44}$H$_{30}$N$_8$O$_{14}$·H$_2$O: C, 57.89; H, 3.53; N, 12.28. Found: C, 58.25; H, 3.52; N, 12.29.

The aqueous supernatant was extracted twice with 100-ml portions of diethyl ether to remove excess benzaldehyde, made basic with 25% aqueous sodium hydroxide, and extracted with three 50 ml portions of benzene. The combined benzene extracts were dried and evaporated to leave 4 g of gummy residue. The latter was triturated with 40 ml of ether–benzene (3:1); the white solid was then filtered, washed with more solvent and dried, 0.24 g (5.5%), mp 270–300°. The extracts were saved (C). This solid was next extracted with 15 ml of boiling benzene to separate the two isomers present.

**A. Benzene-Soluble Isomer.**—Evaporation of the benzene left a solid, mp 280–283°, which melted at 285–286° after recrystallization from 95% ethanol. The analyses, ^{1}H nmr spectrum, solubility behavior, and melting point suggest that this is the *dl* epimer of 4,4'-dibenzal-1,1',4,4'-tetrahydro-1,1'-biisoquinoline, 5a: $\tau$ (CDCl$_3$) 4.39 (s, 1, H$_1$), 2.93 (s, 5, H$_{aromatic}$ in phenyl ring), 2.62–1.72 (m, 4, H$_{aromatic}$), 1.52 (s, 1, benzal methine), 1.06 (s, 1, H$_3$).

*Anal.* Calcd for C$_{33}$H$_{24}$N$_2$: C, 88.04; H, 5.54; N, 6.42. Found: C, 88.08; H, 5.52; N, 6.26; mol wt (mass spectrum) 436.

The picrate was obtained as plates after recrystallization from ethanol, mp 268–269° dec.

*Anal.* Calcd for C$_{44}$H$_{30}$N$_8$O$_{14}$: C, 59.06; H, 3.38; N, 12.52. Found: C, 58.97; H, 3.45; N, 12.66.

**B. Benzene-Insoluble Isomer.**—This compound was purified by dissolving in 20 ml of dimethylformamide, filtering, and adding 100 ml of diethyl ether. The white, microcrystalline powder was filtered, washed three times with ether, three times with water, and vacuum dried for several days at 68° (25 mm, mp 328–329° dec; absorptions due to NH and carbonyl stretching frequencies were absent in the ir spectrum; mass spectrum *m/e* 436 (parent), 218 (M/2, base peak), the peak at *m/e* = 91 which would correspond to the loss of a benzyl fragment was very weak; $\tau$ (CF$_3$COOH) 3.72 (s, 1, H$_1$), 2.70 (s, 5, H$_{aromatic}$ phenyl ring), 1.15–2.05 (m, 4, H$_{aromatic}$), 1.01 (s, 1, benzal methine), 0.45 (s, 1, H$_3$).

The evidence is consistent with those expected for the meso epimer of 4,4'-dibenzal-1,1',4,4'-tetrahydro-1,1'-biisoquinoline 5b.

*Anal.* Calcd for C$_{33}$H$_{24}$N$_2$: C, 88.04; H, 5.54; N, 6.42. Found: C, 87.84; H, 5.66; N, 6.46, 6.36.

Solutions of this compound have a blue-purple fluorescence. Its picrate, obtained from alcohol as long thin needles, decomposed at 317–320°.

**C. 4-Benzal-1,4- (and 3,4-) dihydroisoquinoline.**—The ether–benzene extract (see above) was diluted with 100 ml of n-hexane and chilled; a pale yellow solid (0.9 g, 20%, mp 90–110°) separated. Additional material was isolated as follows. The mother liquors were evaporated and the very gummy residue boiled with 25 ml of cyclohexane; the chilled solution was decanted from about 1 g of tar (discarded) and evaporated. Trituration of this residue with two small volumes of cold n-hexane to remove oily material left more crystalline solid. (The material in these hexane extracts gave a picrate melting at 223–225° after recrystallization from ethanol; a mixture melting point with isoquinoline picrate was not depressed; the ir spectra were identical.) Recrystallization of this solid from n-hexane gave a product melting at 99.5–100.5° (by way of comparison, the melting point of 4-benzylisoquinoline is 119–120°[12]). The parent peak in the mass spectrum was 219; fragments of mass 128 (M − 91) and mass 91 (benzyl) were present but only had very low intensity. The ^{1}H nmr spectrum confirmed the absence of a benzyl group (no benzyl methylene signal), but also suggested that the product was roughly a 2:1 mixture of isomers: (CDCl$_3$) 5.90, 5.62 (2 s, 2 total, protons of methylene group in the nitrogen bearing ring), 2.78 (s, 5, H$_{aromatic}$ in phenyl ring), 2.67–1.85 (m, 4, H$_{aromatic}$), 1.60 (s, 1, benzal methine), 0.8

(8) A. Claus and K. Hoffmann, *J. Prakt. Chem.*, 47 (2), 252 (1893), prepared a dinitroisoquinoline, mp 283.5°, by the action of fuming nitric acid on isoquinoline in fuming sulfuric acid, but did not establish the position of the substituents.

(9) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 93, 1522 (1971).

(10) A proprietary, deuterated solvent made by Stohler Isotope Chemicals, Azusa, Calif.

(11) F. Fortner, *Monatsh. Chem.*, 14, 146 (1893).

(12) M. Avramoff and Y. Sprinsak, *J. Amer. Chem. Soc.*, 76, 4090 (1956).

0.76 (2 s, 1 total, H₁ or H₃ in nitrogen ring, depending on isomeric form).

*Anal.* Calcd for C₁₆H₁₃N: C, 87.64; H, 5.97; N, 6.39. Found: C, 87.76; H, 5.98; N, 6.30.

The picrate after two recrystallizations from 95% ethanol melted at 190–192° (reported[18] for 4-benzylisoquinolinium picrate, 195–196°).

*Anal.* Calcd for C₂₂H₁₆N₄O₇: C, 58.93; H, 3.60; N, 12.50. Found: C, 58.62; H, 3.47; N, 12.17.

Small quantities of two other picrates were also isolated when the crude benzal dihydroisoquinoline was treated with picric acid and the salts were fractionally crystallized. One melted at 229–230° (dec) after recrystallization from ethanol; on admixture with isoquinoline picrate, the melting point was 200–210°.

*Anal.* Calcd for C₃₂H₁₄N₄O₇: C, 59.19; H, 3.16; N, 12.55. Found: C, 59.44; H, 3.22; N, 12.49, 12.47.

A hydrobromide prepared from this picrate decomposed at 308–312° after recrystallization from absolute ethanol; its elemental analyses, like that of the picrate, also suggested a lower hydrogen content than that demanded by a salt of **3** or **4**.

*Anal.* Calcd for C₁₆H₁₂BrN: C, 64.45; H, 4.06; Br, 26.80; N, 4.70. Found: C, 64.57; H, 4.04; Br, 26.63; N, 4.59.

The free base from the bromide partially melted, then resolidified at 157–159°, and finally remelted at 225–230°. The base peak (*m/e*) in the mass spectrum was 217; a small peak at 218 (M + 1) was present but there were no peaks at *m/e* 434–436 (coupled products). Fragments of mass 91 (benzyl) and M − 91 were not present.

The other picrate after recrystallization from acetonitrile decomposed at 266–267°; admixture with the picrate of dibenzal tetrahydrobiisoquinoline, mp 268–269° (see above), depressed the melting point to 245–250°. The ir spectra of these two compounds also differed. Perhaps this compound is the picrate of 4,4′-dibenzyl-1,1′-biisoquinoline, but it was not investigated further.

*Anal.* Calcd for C₄₄H₃₀N₆O₁₄: C, 59.06; H, 3.38; N, 12.52. Found: C, 58.95; H, 3.28; N, 12.49.

**5,5′-Dinitro-1,1′-biisoquinolin e and 5-Nitro-1,1′-biisoquinoline.** —1,1′-Biisoquinoline (8.7 g; 0.039 mol) was nitrated by the procedure of Le Fèvre and Le Fèvre[13] for making 5-nitroisoquinoline. The dried crude product (12.2 g) was dissolved in 2 l. of boiling xylene, filtered from 1.49 of inorganic salts, and chilled to 0°; 8.6 g (72.9%) of dinitro compound was recovered, decomposing at 265–270° after turning black at 250°. A portion was recrystallized from dimethylformamide as pinkish white, feathery needles, melting at 293–294° dec if plunged into a bath preheated to 290°. If heated from room temperature, the compound turned black at 265°, then decomposed at 270–280°: τ (CF₃COCF₃·1.6D₂O) 2.37 (d, 2, H₇, H₈), 1.25 (m, 1, H₆), 1.05 (s, 2, H₃, H₄).

*Anal.* Calcd for C₁₈H₁₀N₄O₄: C, 62.43; H, 2.94; N, 16.18. Found: C, 62.76; H, 2.82; N, 15.78, 15.87.

Evaporation of the xylene left 2.2 g (20.6%) of solid which was recrystallized from 95% ethanol, mp 186–187° dec. The analyses and nmr are consistent with those required for 5-nitro-1,1′-biisoquinoline: τ (CF₃COCF₃·1.6D₂O) 2.65–1.79 (m, 6, H₇, H₇′, H₈, H₈′, H₅′, H₆′), 1.68–1.44 (m, 3, H₆, H₃′, H₄′), 1.28 (s, 2, H₃, H₄).

*Anal.* Calcd for C₁₈H₁₁N₃O₂: N, 13.95. Found: N, 14.04.

(13) C. G. La Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1470 (1935).

# Intramolecular Cyclization of N-Alkyl-3,3',4,4'-tetrahydro-1,1'-biisoquinolinium Salts

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The preparation and chemiluminescence of 2,2'-dimethyl-3,3',4,4'-tetrahydro-1,1'-biisoquinolinium diiodide (1) have recently been described.[1] Although 3,3',4,4'-tetrahydro-1,1'-biisoquinoline (2) very readily forms a monomethiodide, its conversion to the dimethiodide requires more drastic reaction conditions. As a consequence, a competing, intramolecular cyclization, which will be described in this note, also occurs.

When 2 and excess methyl iodide were refluxed in acetonitrile for 18 hr, in addition to 1 (52% yield), there was recovered in approximately 10% yield an isomeric compound whose ¹H nmr spectrum and chemical behavior are consistent with those expected for 7-methyl-5,6,10,11-tetrahydro-8H-diisoquino[1,2-c:2',1'-e]imidazolidiinium diiodide (3). The proton count on 3 indicated only one methyl group. The nmr spectrum was characterized by two other significant changes. One was the appearance of an AB quartet, which, although it is the chemical shift region assigned to 3 and 4 protons in 1,2-dihydroisoquinoline derivatives,[2] is due to the methylene in the imidazole ring, split because of the adjacent asymmetric nitrogen atom in the fused ring system. The other is a marked downfield shift of two of the aromatic ring protons, ascribed to an overlap of the 1,15 protons in the rigid, fused ring system of 3.
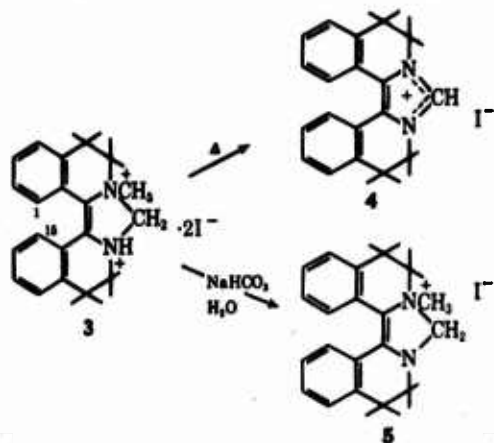


In 1, rotation about the 1,1' bond can still occur and the 8,8' protons do not overlap.

When 3 was heated to 165–170°, both loss of methyl iodide and oxidation occurred to give 5,6,10,11-tetrahydrodiisoquino[1,2-c:2',1'-e]imidazolium iodide (4).

Its ¹H nmr spectrum (see Experimental Section) reflected these changes. Heating an aqueous solution of 3 with sodium bicarbonate yielded the monoquaternary salt 5, whose nmr spectrum, except for one less proton, was the same as that for 3.

It appears that the cyclization which leads to 3 can occur in either of two ways. (1) The monomethiodide of the 1,1'-biisoquinoline cyclizes intramolecularly and the resulting product is further methylated. (2) The dimethiodide 1 is first formed and then undergoes cyclization. There is evidence for both routes. For example, when preformed monomethiodide was refluxed in dry acetonitrile for various lengths of time, the proton nmr spectra on the recovered mixture of salts showed decreasing methyl signals, increasing signals characteristic of a methylene group, and the downfield shift of two aromatic protons as a consequence of the 1,15 proton overlap which develops as the fused ring system forms. Similarly, when 2-benzyl-3,3',4,4'-tetrahydro-1,1'-biisoquinolinium bromide was refluxed in acetonitrile, the benzyl methylene signal disappeared; in addition the generally complicated nmr spectrum of the starting compound (because of unsymmetrical substitution) became simpler and more symmetrical as the cyclization occurred. One of the products recovered from this latter reaction was the 8-phenyl-5,6,10,11-tetrahydrodiisoquino[1,2-c:2',1'-e]imidazolium salt (as the perchlorate).

When purified dimethiodide 1 was refluxed in methanol, ethanol, or 2-propanol, the dark red-orange colored solutions gradually faded. Although the recovered pale yellow product was a difficultly separable mixture, one compound isolated and identified was 5.

2-Benzyl-1,1'-biisoquinolinium bromide remains essentially unchanged under conditions which effect the complete loss of the corresponding 3,3',4,4'-tetrahydro compound. This fact suggests that the greater basicity of the 3,4-dihydroisoquinoline moiety over that of the unreduced isoquinoline is an important factor in the cyclization process. One possible route for cyclization of a monoalkyl salt is depicted in the following simplified scheme.
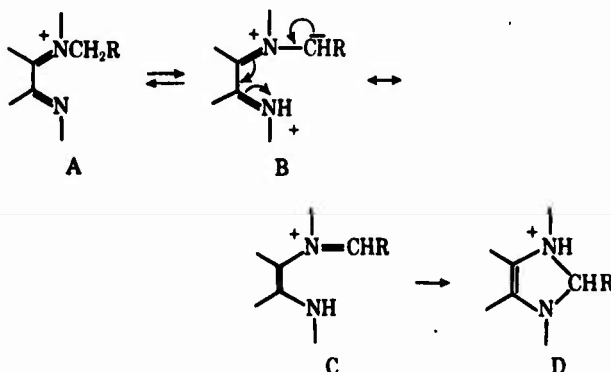


Abstraction of a proton from the alkyl group on A leads to the ylide B, which through charge redistribution gives the immonium salt C. Intramolecular addition of the nucleophile to the latter in a manner

(1) R. A. Henry and C. A. Heller, *J. Luminescence*, 4, 105 (1971).
(2) J. L. Neumeyer, M. McCarthy, K. K. Weinhardt, and P. L. Levins, *J. Org. Chem.*, 33, 2890 (1968).

analogous to the formation of pseudobases from isoquinolinium salts furnishes D. Although proton abstraction from A has been written here as an intramolecular process, it could occur equally well as an intermolecular one. Cyclization by a similar sequence would then give unprotonated D. Only the cis configuration has been shown for C, since it would be the form to cyclize; any trans isomer would through the equilibrium revert to B and ultimately back to cis-C.

This reaction scheme is similar to one proposed for the reduction of bisquaternary 1,1'-biisoquinolinium salts by base to air-reactive olefins.[1,3]

### Experimental Section

**7-Methyl-5,6,10,11-tetrahydro-8H-diisoquino[1,2-c:2',1'-e]-imidazolidiinium Diiodide.**—3,3',4,4'-Tetrahydro-1,1'-biisoquinoline[1] (2, 5.2 g, 0.02 mol) and 8 ml of methyl iodide were refluxed in 100 ml of acetonitrile under a 0° condenser for 18 hr; after the solution had been chilled to 5°, the previously described,[1] dark red dimethiodide was removed, yield 5.7 g (52%).

Addition of ether to the above acetonitrile mother liquors and cooling gave 2.2 g of a mixture of materials. One of these (3), comprising about half of the mixture, was less soluble in 80% ethanol than either the monomethiodide or the dimethiodide (both of which were also present) and after several recrystallizations was obtained as pale purple needles with an orange-red hue. The melting point was very indefinite; partial melting, then resolidification at 160-165° with a change in color from purple to pale yellow. (This new solid decomposed at 240-265°.) When plunged into a hot bath at 190-195°, it completely melted; if plunged into a bath at 165°, it partially melted before resolidifying (see following experiment). This compound in methanol did not chemiluminesce in air when made basic: nmr (DMSO-$d_6$) $\tau$ 6.56 (s, 3, -NCH$_3$), 6.4-7.7 (m, 7), 5.8-6.3 (m, 2, H$_6$, H$_9$), 5.22 (d, 1, $J$ = 7.0 Hz, H$_8$), 4.75 (d, 1, $J$ = 7.0 Hz, H$_8$), 2.57-2.97 (m, 6, H$_2$, H$_3$, H$_4$, H$_{12}$, H$_{13}$, H$_{14}$), 2.10-2.57 (m, 2, H$_1$, H$_{15}$).

*Anal.* Calcd for C$_{20}$H$_{22}$N$_2$I$_2$: C, 44.15; H, 4.07; N, 5.15; I, 46.64. Found: C, 44.38; H, 3.80; N, 5.10; I, 46.75.

When some of 3 was dissolved in a minimum volume of boiling water and treated with excess sodium bicarbonate, cooling gave a pale yellow solid 5. Recrystallization from water furnished coarse yellow needles or prisms, mp 177-178° dec; an aqueous solution had an intense blue fluorescence. The ^{1}H nmr spectrum in DMSO-$d_6$ was almost identical with that for 3 except that the total proton count was one less. Surprisingly, a mass spectrum showed a small parent peak, $m/e$ 416, with the base peak at $m/e$ 290. The presence of a parent peak suggests opening of the imidazole ring by the nucleophile, iodide ion, to give an iodomethylene derivative.

*Anal.* Calcd for C$_{20}$H$_{21}$N$_2$I: C, 57.70; H, 5.08; N, 6.73; I, 30.49. Found: C, 57.85, 57.80; H, 5.03, 5.08; N, 6.62, 6.73; I, 30.64, 30.35.

The monopicrate from 5 melted at 170-171° after two recrystallizations from absolute ethanol.

*Anal.* Calcd for C$_{26}$H$_{24}$N$_5$O$_7$: N, 13.53. Found: N, 13.61.

**Decomposition of 3.**—When 3 was heated for 10 min at 155-165°, there was a 22% loss in weight (theory, 26% for one CH$_3$I); further heating caused very little more loss. Even when heated at 94° (25 mm) there was an 18% loss of weight in 5 days. The crude product decomposed at 240-260°. Recrystallization from 2-propanol gave yellow blades of 5,6,10,11-tetrahydroisoquino-[1,2-c:2',1'-e]imidazolium iodide (4): mp 296-298° dec; nmr (DMSO-$d_6$) $\tau$ 6.83 (t, 4, $J$ = 6.0 Hz, H$_5$, H$_{11}$), 5.67 (t, 4, $J$ = 6.0 Hz, H$_6$, H$_{10}$), 2.5-2.9 (m, 6, H$_2$ H$_3$, H$_4$, H$_{12}$, H$_{13}$, H$_{14}$), 2.05-2.36 (m, 2, H$_1$, H$_{15}$), 0.70 (s, 1, CH in imidazolium ring, H$_8$).

*Anal.* Calcd for C$_{19}$H$_{17}$N$_2$I: C, 57.01; H, 4.28; N, 7.00; I, 31.71. Found: C, 56.80; H, 4.36; N, 6.93; I, 32.10.

The picrate decomposed at 241-242°.
*Anal.* Calcd for C$_{25}$H$_{19}$N$_5$O$_7$: N, 13.97. Found: N, 14.00.

**Decomposition of 1 in Methanol.** A solution of 0.86 g of 1 in 100 ml of absolute methanol was refluxed for 26.5 hr while protected from moisture. The initially dark red-orange solution became pale orange in color. Cooling for 2 days at 5° deposited 0.36 g of starting compound, mp 208-209° dec; an additional 0.15 g was recovered by evaporating the mother liquors to 20 ml and cooling. Further evaporation to 4-5 ml and cooling gave a mixture of 1 and yellow needles, mp *ca.* 150°, which were separated mechanically. Additional amounts of the latter compound can be isolated by reworking the mother liquors. Recrystallization from 2-propanol gave pale yellow needles, mp 166-167°; the ^{1}H nmr indicated a mono-2-propanolate. A sample was desolvated at 70° (25 mm) for 24 hr prior to analysis. The nmr spectrum and the analytical data agree with those for 5.

*Anal.* Calcd for C$_{20}$H$_{21}$N$_2$I: C, 57.70; H, 5.08; N, 6.73; I, 30.49. Found: C, 57.46; H, 5.05; N, 6.67; I, 30.56.

**5,6,10,11-Tetrahydro-8-phenyldiisoquino[1,2-c:2',1'-e]-imidazolium Perchlorate.**—2-Benzyl-3,3',4,4'-tetrahydro-1,1'-biisoquinolinium bromide[1,4] (0.76 g) in 25 ml of acetonitrile was refluxed for 72 hr. The cooled solution was diluted with a large volume of ether to precipitate a hygroscopic, amorphous solid which was filtered and dried, mp 110-150°; the ^{1}H nmr spectrum in either CDCl$_3$ or DMSO-$d_6$ revealed the complete disappearance of the benzyl methylene signal. Since attempts to recrystallize this product were unsatisfactory, it was dissolved in a small volume of water, filtered from insoluble material, and converted to the perchlorate by adding excess sodium perchlorate. This salt, when dry, was easily recrystallized from 2-propanol. The cream-colored crystals turned dark at *ca.* 270° and decomposed at 283-285°; nmr (CDCl$_3$) $\tau$ 6.87 (t, 4, $J$ = 6.5 Hz, H$_5$, H$_{11}$), 5.83 (t, 4, $J$ = 6.5 Hz, H$_6$, H$_{10}$), 2.60 (s, 5, phenyl), 2.16-2.70 (m, 6, H$_2$, H$_3$, H$_4$, H$_{12}$, H$_{13}$, H$_{14}$), 1.94-2.16 (m, 2, H$_1$, H$_{15}$).

*Anal.* Calcd for C$_{25}$H$_{21}$ClN$_2$O$_4$: Cl, 7.89; N, 6.24. Found: Cl, 7.50; N, 6.11.

**2-Benzyl-1,1'-biisoquinolinium Bromide.**—1,1'-Biisoquinoline (0.6 g) and benzyl bromide (0.4 g) (equimolar ratio) in 10 ml of dry acetonitrile stood at room temperature for 6 days. The former compound gradually dissolved as benzylation occurred. Addition of ether precipitated the monoquaternary salt, which was recrystallized twice from 2-propanol as needles, mp 136-137° dec. The nmr spectrum indicated one propanol of crystallization. The desolvated compound decomposed at 195-197°: nmr (DMSO-$d_6$) $\tau$ 4.18 (s, 2, benzyl CH$_2$), 2.35-3.22 (complex multiplet, 9, benzyl C$_6$H$_5$, H$_5'$, H$_6'$, H$_7'$, H$_8'$), 2.67 (d, 1, $J$ = 7.0 Hz, H$_5$), 2.14 (t, 1, $J$ = 7.0 Hz, H$_6$), 1.73 (t, 1, $J$ = 7.0 Hz, H$_7$), 1.64 (d, 1, $J$ = 5.5 Hz, H$_4'$), 1.37 (d, 1, $J$ = 7.0 Hz, H$_8$), 1.11 (d, 1, $J$ = 5.5 Hz, H$_3'$), 0.97 (d, 1, $J$ = 7.0 Hz, H$_4$), 0.62 (d, 1, $J$ = 7.0 Hz, H$_3$).

*Anal.* Calcd for C$_{25}$H$_{19}$BrN$_2$·C$_3$H$_8$O: C, 68.99; H, 5.58; Br, 16.39; N, 5.75. Found: C, 69.11; H, 5.40; Br, 16.55; N, 5.77.

Refluxing some of the desolvated salt in dry acetonitrile for 72 hr caused no change; the recovered product melted at 194.5-196° and its nmr spectrum was the same as that of the starting material.

**Registry No.**—1, 34414-11-4; 3, 34410-07-6; 4, 34414-12-5; 4 monopicrate, 34414-13-6; 5, 34414-14-7; 5 monopicrate, 34414-15-8; 5,6,10,11-tetrahydro-8-phenyldiisoquino[1,2-c:2',1'-e]imidazolium perchlorate, 34414-16-9; 2-benzyl-1,1'-biisoquinolinium bromide, 34414-17-0.

(3) C. A. Heller and R. A. Henry, unpublished work.
(4) Nmr (DMSO-$d_6$) $\tau$ 6.90 (t, 2, $J$ = 7.5 Hz, H$_4'$), 6.25-6.72 (m, 2, H$_{4eq}$, H$_{4ax}$), 6.10 (t, 1, $J$ = 10.0 Hz, H$_{3ax}$), 5.82 (doubled triplet, 2, $J_t$ = 7.5 Hz, $J_d$ = 3.0 Hz, H$_3'$), 5.60 (m, 1, H$_{3eq}$), 4.55 (s, 2, benzyl CH$_2$), 2.08-2.70 (m, 5, benzyl C$_6$H$_5$).

TECHNICAL REPORT NO. 1

The Chemiluminescent Autoxidation of Reduced

Biisoquinolinium Dications

Carl A. Heller, Ronald A. Henry and John M. Fritsch

# THE CHEMILUMINESCENT AUTOXIDATION OF REDUCED

# BIISOQUINOLINIUM DICATIONS

**Carl A. Heller** and Ronald A. Henry

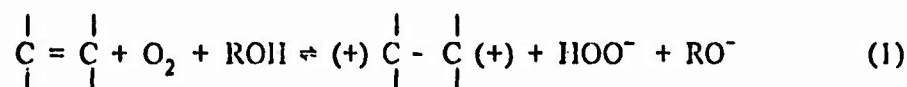Naval Weapons Center (Code 605), China Lake, CA 93555

**John M. Fritsch**

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## INTRODUCTION

Numerous chemiluminescent reactions involve molecular oxygen or hydrogen peroxide reacting with an organic compound. In many cases the formation of an intermediate 1,2-dioxetane can be demonstrated or is implicated as one of the steps in the reaction mechanism. The excitation step then involves splitting the dioxetane ring to form two carbonyl groups. The excitation energy is sometimes found in the carbonyl compounds and sometimes in a convenient fluorescer.

The reaction by which the dioxetane ring is formed for any class of compounds is of interest. This is particularly true when the reaction proceeds from ground state $O_2$. We have studied two classes of electron-rich olefins which oxyluminesce and which are catalyzed by alcohols.[1,2] The initiating reaction is proposed[1] to be of the type:

$$\overset{|}{\underset{|}{C}} = \overset{|}{\underset{|}{C}} + O_2 + ROH \rightleftharpoons (+) \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} (+) + HOO^- + RO^- \qquad (1)$$

The equilibrium position of reaction 1 will depend upon the reduction potential of the olefinic compound and upon the concentration of ROH. Once peroxy anion is formed, the reaction with dication to form dioxetanes should proceed as with base-catalyzed $H_2O_2$ reactions.

1

Tetraaminoethylenes, which are air reactive and some of which chemiluminesce, have large reduction potentials; for example, that of tetrakisdimethylaminoethylene (TMAE), is comparable to that of zinc. Mason and Roberts[3] suggested that biisoquinolinium (BIQ) salts, which chemiluminesce when made basic in air, first react to form olefins. We have previously described the reduction and subsequent autoxidation of one BIQ salt.[2] In this paper we want to describe the reactions of 8,9-dihydropyrazino-[1,2-a:3,4-a'][1,1']-biisoquinolinium dibromide monohydrate (BIQ I⁺⁺), whose chemiluminescence was the brightest of the several salts studied by Mason and Roberts. In the next section we will describe how BIQ I⁺⁺ is reduced to a mixture of olefins. The subsequent section describes the chemiluminescent autoxidation reaction.

## FORMATION AND PROPERTIES OF THE OLEFINS

The reduction by base of BIQ I⁺⁺ would be expected to be similar to that of the more frequently studied bipyridinium dications such as Diquat and Paraquat. Two very different mechanisms[4,5a,5b,6] have been advanced for these reductions. Our results support a proton abstraction mechanism as opposed to reduction by the methoxide-formate anion redox couple.

Reduction of the BIQ I⁺⁺ at a Pt electrode gives two clean, reversible, one-electron additions. The expected products[6,7,8,9] would be the following:
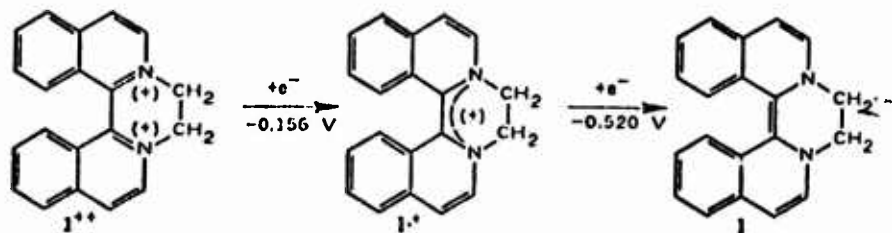


The product I·⁺ was red.

The reduction potentials were measured versus an s.c.e. in acetonitrile using tetraethylammonium perchlorate as supporting electrolyte. The results mean that I is a somewhat weaker reducing agent than 1,1'-dimethyl-1,1'-dihydro-4,4'-bipyridyl.[6,7] We can use the reduction potentials to calculate an equilibrium constant for the reaction

$$I^{++} + I \rightleftharpoons 2I^{\cdot +} \tag{2}$$

of K = 1.43 × 10⁶. This large constant suggested that the radical should be

formed quite readily if I⁺⁺ or I were present with trace amounts of reducing or oxidizing materials.

It has indeed proven simple to obtain I·⁺. Methanol solutions of I⁺⁺ in Pyrex or soft glass vessels under $N_2$ slowly change from yellow to wine-red, and an EPR signal appears. Figure 1 shows the visible absorption spectrum, and Fig. 2 shows the EPR spectrum. The same spectra are obtained from methanol or water solutions of I⁺⁺ in contact with Zn powder. The color and EPR signal disappear if $O_2$ is added, but the amount of I⁺⁺ is little affected.

Solutions in methanol under $N_2$ do not form I·⁺ if in N51A neutral glass vials, nor do aqueous solutions in Pyrex turn wine-red. This probably indicates that basic properties of the glass, as well as trace reducing materials, will give the radical. The following experiments show the mechanism of reduction by strong base.

If sodium methoxide is added in less than stoichiometric amounts to a methanol solution of BIQ I⁺⁺ under $N_2$, the solution changes to orange, but the typical I·⁺ spectrum remains under the new absorbance. If sodium methoxide is added in excess to the wine-red or yellow solution under $N_2$, it turns orange-red and the EPR signal disappears. The visible absorbance spectrum is shown in Fig. 1. This orange-red solution reacts with $O_2$ to give chemiluminescence and the bis-isoquinolones shown in Fig. 3; A and C have been isolated and their structures determined (see appendix). These two products would be expected from the autoxidation of olefins I and III, shown in Fig. 4.
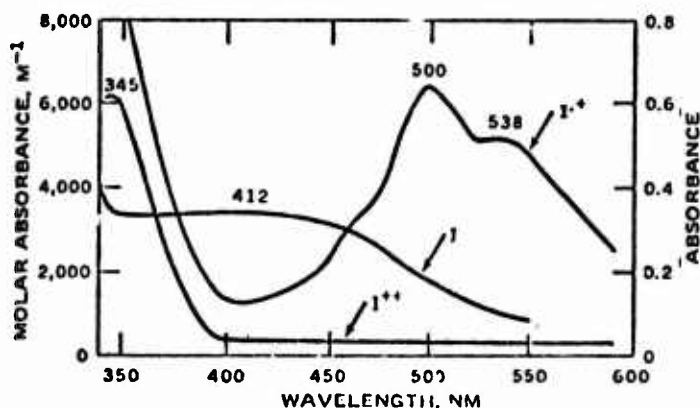


FIG. 1. Absorbance Spectra of Three Solutions. I⁺⁺ is BIQ I⁺⁺ in methanol under air (left scale); yellow solution. I is same solution made basic with NaOMe (left scale); orange-red solution. I·⁺ is first solution after standing under $N_2$ (right scale); wind-red solution.
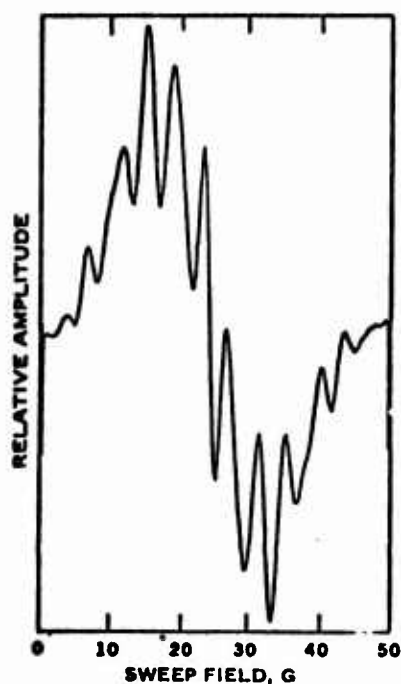
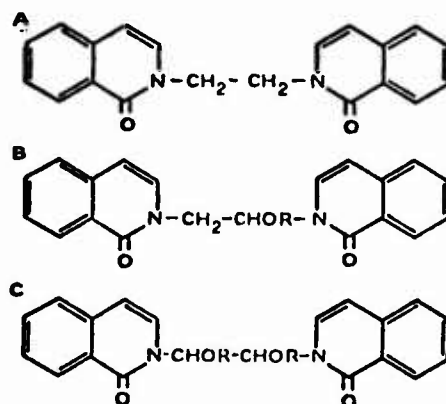FIG. 2. EPR Spectrum of I·* in Methanol, With g = 2.0025. Spectrum run by D. W. Moore and W. Thun.



FIG. 3. Bis-isoquinolones Found or Expected From Autoxidation of BIQ I*.

The mass spectrometric data in Tables 1 and 2 show evidence for all the olefins of Fig. 4, as well as for the bis-isoquinolones of Fig. 3. Traces of $O_2$ account for these oxidation products. These mass spectrometric samples were prepared under $N_2$ in the small cavity of the quartz solid-sample holder of the Hitachi RMU-6E mass spectrometer. A small sample of BIQ I* was placed in the cavity. Zinc powder was added to two samples and then either water or methanol. After the samples were thoroughly dried by evacuation, they were transferred to the Hitachi with a short exposure to air. Similar samples were
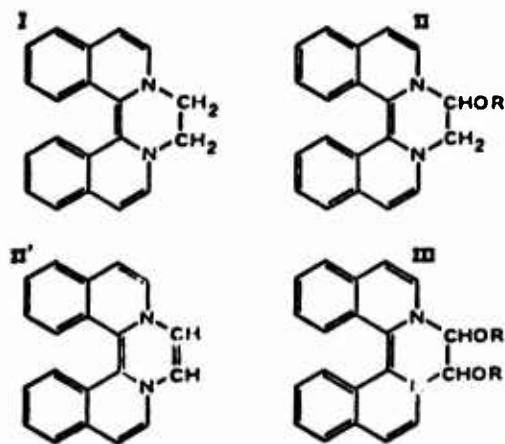
4

FIG. 4. Reduced Forms of BIQ I Dication.

TABLE 1. Mass Spectra of Species Formed in Methanol Under $N_2$.

| Mass | Intensity[a] | Intensity[b] | Species[c] |
|------|------|------|------|
| 255 | 137.1 | 144 | ... |
| 269 | 8.3 | 19.7 | ... |
| 282 | 2.2 | 13.4 | II' |
| 283 | 6.6 | 16.3 | ... |
| 284 | 51.1 | 52.2 | I |
| 299 | ... | 5.52 | ... |
| 314 | ... | 48.1 | II |
| 315 | ... | 12.9 | ... |
| 316 | 0.56 | 9.4 | A |
| 329 | ... | 13.3 | ... |
| 330 | ... | 3.9 | ... |
| 331 | ... | 36.9 | ... |
| 344 | ... | 25.0 | III |
| 345 | ... | 7.2 | ... |
| 346 | ... | 12.5 | B |
| 361 | ... | 1.1 | ... |
| 362 | ... | 0.6 | ... |
| 376 | ... | 0.97 | C |
| 408 | ... | 0.15 | C·CH$_3$OH or III·2CH$_3$OH |

[a] BIQ I$^{++}$ + Zn + CH$_3$OH. CH$_3$OH quickly evaporated from sample.
[b] BIQ I$^{++}$ + NaOCH$_3$ (1.0 M). CH$_3$OH quickly evaporated from sample.
[c] R is CH$_3$ in formulas of Fig. 3 and 4.

TABLE 2. Mass Spectra of Species Formed in Water.

| Mass | Intensity[a] | Species[b] |
|------|------|------|
| 255 | 138.0 | ... |
| 256 | 72.9 | ... |
| 269 | 2.0 | I - 15 |
| 270 | 0.73 | ... |
| 271 | 0.80 | ... |
| 272 | 0.74 | ... |
| 282 | 0.5 | Fragment of I, no II' |
| 283 | 2.0 | ... |
| 284 | 6.4 | I |
| 285 | 2.2 | ... |
| 286 | 3.5 | ... |
| 300 | 0.14 | Trace of II |
| 302 | 3.82 | Fragment of III - 14 |
| 303 | 0.60 | ... |
| 316 | 5.10 | III (A unlikely) |
| 317 | 1.12 | ... |

[a] BIQ I$^{++}$ + NaOH (1.0 M). Water quickly evaporated from sample.
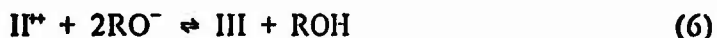[b] R is H in formulas of Fig. 3 and 4.

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prepared by adding sodium methoxide or sodium hydroxide solutions to the salts.

The solid samples were run at 220, 240, and 250°C. The zinc-treated samples gave nearly identical spectra whether wet with water or methanol. The parent peaks indicate I and a trace of A. The basic methanol solutions produced I, II', II, and III with some A, B, and C (with R = CH$_3$). Aqueous NaOH, in which the olefins precipitate rapidly, gave mainly I and III (with R = H). This reduction in aqueous solutions seems to rule out the methoxide ion reduction mechanism for these compounds.[5a,5b]

Other mass spectrometric samples were made by evaporating basic solutions which had stood for hours or days. The spectra were more complex than those in Tables 1 and 2. It appears that the olefins react further in basic solution, giving species with still higher masses and with intermediate masses. These results are consistent with the slow color changes and with a changing quantum yield of the oxyluminescent reaction as the solutions age. We have not investigated these complex, slow changes.

The complete sequence of reactions to produce compounds like I, II, II', and III has been discussed elsewhere.[2] A simplified sequence would be

$$I^{++} + 2RO^- \rightleftharpoons II + ROH \qquad (3)$$

$$I^{++} + 2RO^- \rightleftharpoons II' + 2ROH \qquad (4)$$

$$II + I^{++} \rightleftharpoons II^{++} + I \qquad (5)$$

$$II^{++} + 2RO^- \rightleftharpoons III + ROH \qquad (6)$$

This reaction scheme would produce the reduced species found in our mass spectral analysis.

It seems reasonable that the bipyridinium and biquinolinium compounds will react analogously. As mentioned above, our mechanism agrees generally with that of Corwin and others[4] for the 1,1'-dibenzyl-4,4'-bipyridinium dication. In presenting the evidence for reduction by the methoxide-formaldehyde redox couple, the appearance of formaldehyde from dimethyl bipyridinium dication was important.[5a] However, Urry and Sheeto[10] have shown that formaldehyde can arise from a methylamino group in octamethyloxamidinium dication following proton abstraction. Furthermore, the methoxide-formaldehyde couple has too low a redox potential for the observed reductions to olefins.[6]

6

Our evidence shows clearly that proton abstraction is the important initial mechanism for reduction of BIQ I[+] to the mixed olefins. Along with the earlier work,[4] it suggests that a similar mechanism should be reconsidered for dimethyl bipyridinium dications. Perhaps the bridged bipyridinium dications recently studied by Black and Summers[11] would be useful to test the mechanistic points.

We have observed that when aqueous NaOH solution is added to an aqueous solution of BIQ I[+], a red precipitate of I and III is formed, even in air. The mass spectra of the precipitate were similar to those of Table 2. Compounds II or II′ are nearly absent, although our mechanism shows them as primary products. The reasonable explanation for their absence is that II is a stronger reducing agent than I, so that the equilibrium of reaction (5) is to the right. Reaction (5), being ionic, should be rapid—more rapid than the autoxidation, which explains why we see no light from the aqueous system. Probably III would be a still stronger reducing agent.

We could not isolate II, II′, or III for a direct measurement of their oxidation or reduction potentials. We did prepare a tetramethoxy BIQ according to the method of Mason and Roberts.[3,12]
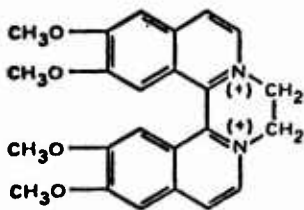


It has reduction potentials of −0.43 and −0.70 V versus an s.c.e. in acetonitrile.[9] The presence of electron-donating $CH_3O$ groups on the aromatic ring would be expected to increase the reduction potentials. Apparently, OH or OR groups on a carbon atom alpha to the nitrogen in the pyrazino ring have a similar effect.

Olefin I has recently been synthesized by an alternate route by W. H. Urry of the University of Chicago; its solution shows the EPR spectrum of I[.+] and oxyluminesces to form bis-isoquinolone A (m.p. 195 to 197°C).[13]

## General

The oxidation of BIQ I++ in basic methanol is fast (about 90% of the light appears in 10 sec) and therefore bright, even though the violet light has a poor photopic factor. As an air-reactive material it seems to have possible applications in automatic emergency light systems if the emission could be red-shifted by suitable changes. Since it was not possible to separate the mixed olefins prepared under nitrogen by reduction of BIQ I++ by either base or zinc powder (previous section), most of the studies reported here are for the equilibrium mixture of olefins obtained from BIQ I++ and $NaOCH_3$ in air-saturated methanol.

## Fluorescence Spectra and Quantum Yields of Products

The major products formed when $NaOCH_3$ solution is added to BIQ I++ in air are the bis-isoquinolones A and C. The separated compounds have been studied in a Turner Model 210 spectrofluorometer, which produces corrected spectra.[14] The fluorescence emission spectra of A and C are shown in Fig. 5. For A the peaks are at 370 and 385 nm, with a height ratio of 1.00/0.96. For C the peaks are at 374 and 388 nm, with a height ratio of 0.97/1.00.
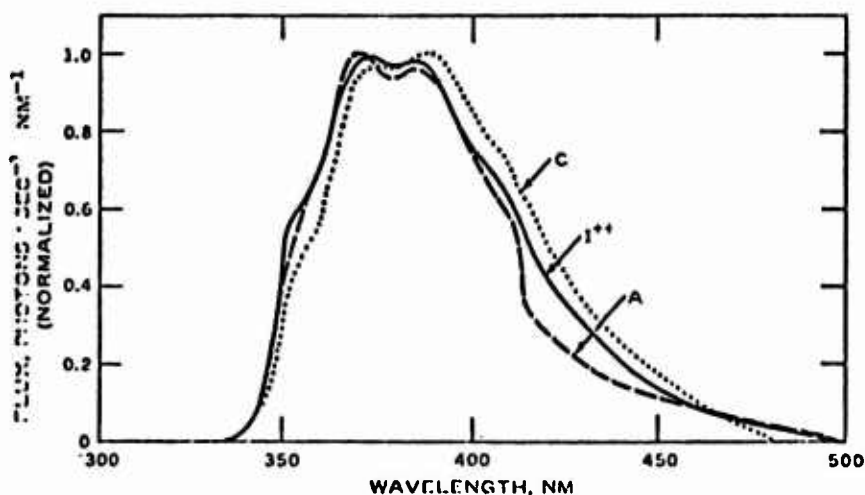


FIG. 5. Spectra for Comparison. I shows chemiluminescence of BIQ I++. [I++] = $10^{-4}$ M in methanol. A and C show fluorescence of bis-isoquinolones A and C in methanol. [A] = 2.17 x $10^{-4}$ M. [C] = 1.17 x $10^{-4}$ M.

Quantum yields were measured versus quinine sulfate under air at 700 torr. The measured yields for A and C are 0.04 and 0.069, while a product mixture in basic methanol gave 0.042. The product mixture was also measured under $N_2$ where we obtained 0.047, or a Stern-Volmer constant of $K = 0.91 \times 10^{-3}$ torr$^{-1}$, if we considered the quenching to be linear. The bis-isoquinolone spectra change somewhat with aging in solution.

### Chemiluminescent Emission Spectra

A flow system was built to produce a constant luminescence in a flow cell in the fluorometer. BIQ I$^{++}$ and NaOCH$_3$ solutions were mixed just outside the cell. The time interval of the reaction irradiating the monochromator was determined by the flow rate and cell size.

At the shortest possible time, the chemiluminescent emission was as shown in Fig. 5. This would appear to be due to A*, with some C* possibly included. The difficulty of a positive identification was due to the spectral shift shown in Fig. 6. If the flow rate was slowed, a different spectrum appeared, with a maximum around 418 nm. This was dim enough to require a wide slit, so we got little resolution. This 418-nm peak was not found in fluorescence of the reaction product.
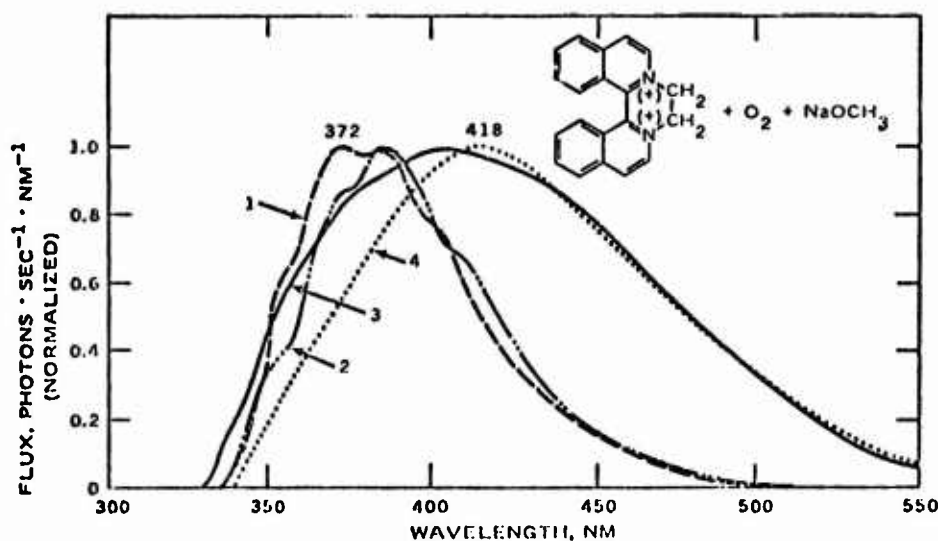


FIG. 6. BIQ I$^{++}$ Chemiluminescence Showing Spectral Change During Autoxidation. Spectra were obtained from flow cells in a spectrofluorometer (without excitation). Reaction was initiated by flowing together solutions of BIQ I$^{++}$ ($2 \times 10^{-4}$ M) and NaOCH$_3$ ($10^{-2}$ M) in about 1:1 ratio. Spectrum 1 taken from 0.14-ml cell using 60-ml $\cdot$ min$^{-1}$ flow and 10-nm slit. Spectrum 2 taken from 2-ml cell using 60-ml $\cdot$ min$^{-1}$ flow and 2.5-nm slit. Spectra 3 and 4 taken from 2-ml cell using slow but undetermined flow rates and 25-nm slit.

## Kinetic Measurements

It was possible to stop the flow through the fluorometer cell and to monitor the decay of light at any one wavelength. Figure 7 shows one such run plotted as first-order decay curves. Monitoring at 375 nm would give only one curve. All runs gave similar first-order decay kinetics with good straight lines. However, the decay slopes were poorly reproducible, which may have been due to the effects of moisture or other impurities.

At 25°C the rate constants were $k' = 0.17 \pm 0.11$ sec$^{-1}$ and $k'' \cong 0.01$ sec$^{-1}$. An Arrhenius plot of runs at 25° and 2 to 3°C gave an activation energy of $E' \cong 10$ kcal mole$^{-1}$ for $k'$. The value of $E'$ was somewhat larger. Thus there are two reactions occurring to give the two types of emission. This would seem to involve two intermediates as well as two products. If either of these decay rates are for dioxetanes, they are clearly faster than those for the more stable alkyl or alkoxy dioxetanes. For those the room-temperature rate constants are about $10^{-4}$ sec$^{-1}$ and the activation energies about 20.[15,16]
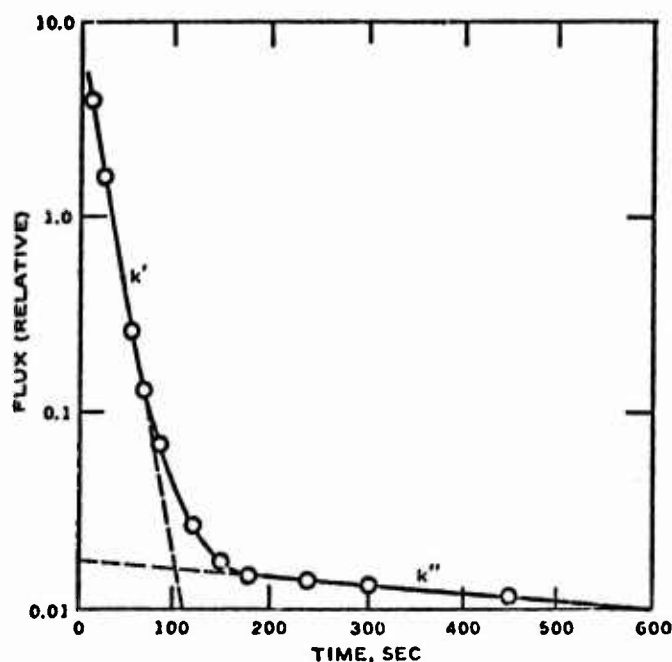


FIG. 7. Decay Kinetics of Light Monitored at 430 nm With 25-nm Slit. Conditions: [BIQ I⁺] = 1.05 × 10$^{-4}$ M; [NaOCH$_3$] = 50 × 10$^{-4}$ M; T = 2.3 to 2.5°C. Results: $k' = 60 \times 10^{-3}$ sec$^{-1}$; $k'' = 4 \times 10^{-3}$ sec$^{-1}$.

Since the plot in Fig. 7 is semilog, it is clear that most of the light comes from the fast reaction; that is, the area under k″ is only a few percent of that under k′.

## Quantum Yield Effects

Earlier we reported the absolute chemiluminescent quantum yields of BIQ I⁺ under carefully controlled conditions.[17] Using the same apparatus, we have measured approximate quantum yields to study the effect of temperature, $O_2$ pressure, and initial concentration of BIQ I⁺. These are overall quantum yields defined as $\bar{q} = \int F dt/n_i$, where F is flux, $\int F dt$ is the graphically integrated light output in einsteins, and $n_i$ is initial moles of BIQ I⁺.

Although temperature affects the rate of light output, it has little effect on $\bar{q}$ (Table 3). This probably means that there is no dark reaction path in competition with the light-producing reaction path. Only if both paths fortuitously had equal activation energies would $\bar{q}$ remain constant over a 78°C range.

**TABLE 3.** Effect of Temperature on $\bar{q}$.

[BIQ I⁺] ≈ $10^{-4}$ M;
[N₂OCH₃] ≅ 0.1 M.

| T, °C | $\bar{q}$, einstein · mole⁻¹ |
|-------|------------------------------|
| 0     | 0.0114                       |
| -30   | 0.0110                       |
| -78   | 0.0132                       |

The $O_2$ results (Table 4) show some effect and perhaps a balancing of kinetics and quenching. However there is no strong, single effect of $O_2$ pressure on $\bar{q}$.

The effect of initial concentration of BIQ I⁺ is perhaps the most revealing (Table 5). It shows that the differential quantum yield defined as $q = (dF/dt)/(dn/dt)$ must equal the overall yield $\bar{q}$. This in turn means that q must be constant over the run and not depend upon [I⁺], [$O_2$], or temperature. This implies a mechanism without dark reactions or strongly competing light paths. This is very different from TMAE, where both [TMAE] and [$O_2$] affect q strongly.

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**TABLE 4. Effect of O$_2$ Pressure on $\bar{q}$.**

[BIQ I$^+$] $\approx$ 10$^{-4}$ M; [NaOCH$_3$] $\approx$ 0.1 M; T = 0°C.

| P$_{O_2}$, torr | $\bar{q}$, einstein · mole$^{-1}$ |
|---|---|
| 66.3 | 0.0068 |
| 121.6 | 0.0079 |
| 125.7 | 0.0079 |
| 243.3 | 0.0065 |
| 614 | 0.0061 |

**TABLE 5. Effect of Initial BIQ I$^+$ Concentration on $\bar{q}$.**

[NaOCH$_3$] $\approx$ 0.1 M; T = –78°C.

| [BIQ I$^+$], M | $\bar{q}$, einstein · mole$^{-1}$ |
|---|---|
| 10$^{-5}$ | 0.0122 |
| 10$^{-4}$ | 0.0122 |
| 5 X 10$^{-4}$ | 0.0117 |

## SUMMARY

The reaction of BIQ I$^+$ with base produces two olefins as the main products. These olefins react rapidly with O$_2$ or basic H$_2$O$_2$.[2,3] The major products are two bis-isoquinolones corresponding to O$_2$ addition across the olefinic double bond and subsequent splitting. Most of the light emitted comes from the excited bis-isoquinolones, but there is a slow reaction producing light at 418 nm.

The reaction is simple in the sense that $\bar{q}$ = q and there seem to be no competing reactions with different kinetic rates or activation energies. Any intermediates are unstable, and in particular any dioxetane intermediate decomposes with higher rates and lower activation energies than are common. These same high rates also hold for TMAE, suggesting that the electron-donating groups are responsible for the high reactivity of the dioxetane.

Since olefins can now be synthesized directly as single species,[13] the chemiluminescent autoxidation of pure compounds can now be studied.

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# APPENDIX

## Isolation and Characterization of Oxidation Products

8,9-Dihydropyrazino-[1,2-a: 3,4-a'][1,1']-biisoquinolinium dibromide (0.5 g) was dissolved in 400 ml of absolute methanol and treated with 1.0 g of sodium methoxide (approximately 10-fold excess) in 100 ml of methanol. The red-orange colored solution first became deep blue, then rapidly changed to red-brown. Dry air was aspirated through the solution for 4 hours; the color faded to yellow in about 1 hour. The solution was evaporated to dryness under reduced pressure at ambient temperature, and the solid residue extracted several times with diethyl ether. Evaporation of the extracts left 0.3 g of off-white solid, m.p. 100 to 150°C. (An additional 0.1 g was recovered by slurrying the ether-insoluble residue with water and filtering.)

The crude product was dissolved in 10 ml of hot 50% aqueous ethanol and cooled slowly to 25°C; two different types of crystals formed, which were easily separated mechanically:

1. Coarse prisms, m.p. 200 to 202°C, after a second recrystallization from 50% ethanol; reported[1][2] for 1,2-di-(N-isoquinolon-1-yl)ethane, 203 to 205°C: mass spectrum $m/e$ (rel. intensity) 316 (parent, 10), 188 (19), 171 (2-vinyl-isoquinolone-1, a McLafferty rearrangement product, 100), 170 (66), 158 (M/2, 6), 145 (1-hydroxyisoquinoline, the other McLafferty rearrangement product, 13), 128 (63); nmr (CDCl$_3$) $\tau$ 5.60 (s, 2, C$\underline{H}_2$ in ethylene bridge); 3.65 (d, 1, $\underline{J}$ = 7 Hz, H$_4$); 3.12 (d, 1, $\underline{J}$ = 7 Hz, H$_3$); 2.28-2.60 (m, 3, H$_5$, H$_6$, H$_7$); 1.45 (m, 1, H$_8$).

2. Felted needles, m.p. 190 to 191°C, after two more recrystallizations from 50% ethanol. The data are consistent with those required for 1,2-dimethoxy-1,2-di-(N-isoquinolon-1-yl)ethane: mass spectrum $m/e$ (rel. intensity) 376 (parent, 9), 232 (53), 231 (2-dimethoxyvinylisoquinolone-1, a McLafferty rearrangement product, 7), 198 (M/2, symmetrical bond cleavage between carbon atoms bearing the methoxyl groups, 100), 185 (15), 171 (22), 170 (M/2-CO, 21), 160 (12), 145 (1-hydroxyisoquinoline, the other McLafferty rearrangement product, 7), 128 (98). None of the processes lead to fragments with methoxy on the ring. Nmr (CDCl$_3$) $\tau$ 6.52 (s, 3, C$\underline{H}_3$O-), 3.43 (s, 1, CH$_3$OC$\underline{H}$-), 3.38 (d, 1, $\underline{J}$ = 6.5 Hz, H$_4$), 2.22-2.60 (m, 4, H$_3$, H$_5$, H$_6$, H$_7$,), 1.55 (m, 1, H$_8$).
Anal. Calcd. for C$_{22}$H$_{20}$N$_2$O$_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 70.97; H, 5.39; N, 7.34.

13

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13. ABSTRACT

The syntheses of various 1,1'-biisoquinoline derivatives and salts are described; some of the unusual chemistry encountered in the preparative effort is discussed.

When aqueous or alcoholic solutions of these 1,1'-biisoquinolinium salts are made basic while exposed to air, bright chemiluminescence occurs. The intensity and duration of the light depends on the particular salt. Oxidation products have been isolated, their structures determined, and their fluorescence correlated with the light emitted during chemiluminescence. A mechanism has been proposed for the oxyluminescence reaction which involves reduction of the biisoquinolinium dication by hydroxide or alkoxide ion to an air-reactive, electron-rich olefin. Oxidation-reduction potentials for the dication--ion radical--olefin system have been determined.

Chemiluminescence quantum yields have been measured, and factored into fluorescence efficiencies and chemical efficiencies.

| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
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| Biisoquinolines | | | | | | |
| Quantum yields | | | | | | |
| Energy conversion | | | | | | |

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The syntheses of various 1,1'-biisoquinoline derivatives and salts are described; some of the unusual chemistry encountered in the preparative effort is discussed.

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biisoquinolinium salts are made basic while exposed
to air, bright chemiluminescence occurs. The inten-
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ticular salt. Oxidation products have been isolated,
their structures determined, and their fluorescence
correlated with the light emitted during chemilu-
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oxyluminescence reaction which involves reduction of
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